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Technical Considerations for De Minimis Pollutant Transport through Polymeric Liners

Environmental Protection Polymers, Inc.
Hawthorne, CA

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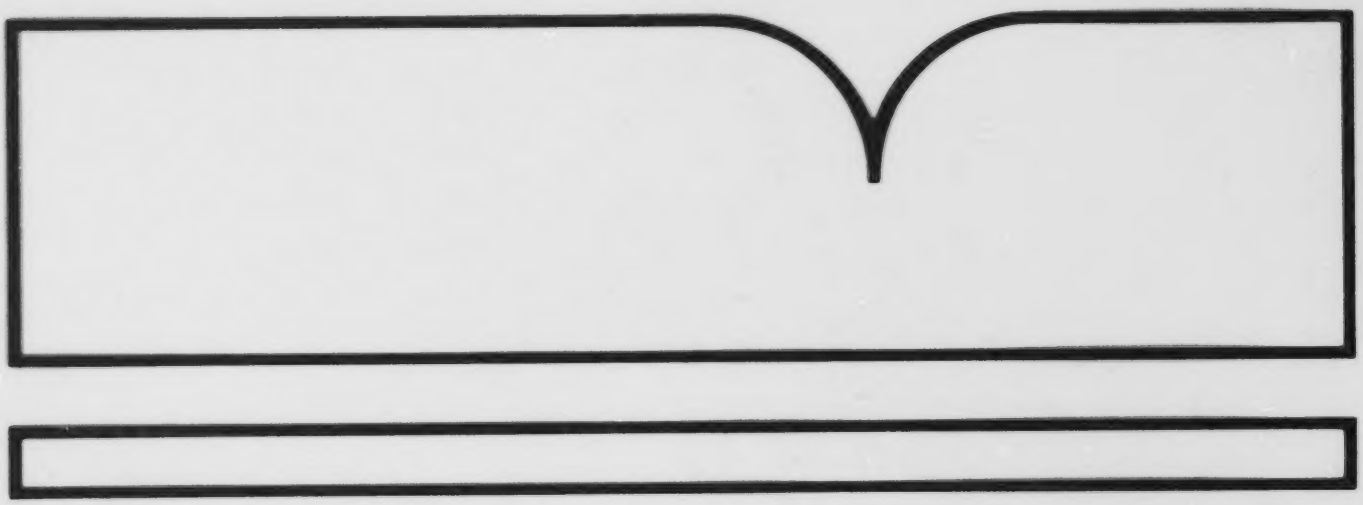

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TECHNICAL CONSIDERATIONS FOR DE MINIMIS POLLUTANT TRANSPORT THROUGH POLYMERIC LINERS

by

R. W. Telles, S. L. Unger and H. R. Lubowitz

Environmental Protection Polymers, Inc.
Hawthorne, California 90250

Contract No. 68-03-3218

Project Officer

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16. ABSTRACT

This report provides a technical basis for assessing the transport of fluids through polymeric liners used to confine pollutants in landfills and impoundments. When a mixture of organic fluids, water, salts, and other substances are confined by an intact liner, first the orgnaic fluids permeate according to their mobilities, then water. Salts, macromolecules, and microorganisms remain confined. These phenomena indicate that fluids are transported by the permeation mechanism and that properly selected and installed liners made with commodity resins can be effective. Organic fluids can be one of the major factors in determining de minimis values. These permeation rates can be appreciable; therefore, impoundments with organic fluids must be selectively designed so that adequate protection of health and the environment is maintained.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of the State and local governments, and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report provides technical considerations regarding performance of polymeric liners in hazardous waste landfills and surface impoundments. Specifically, the considerations relate to pollutant transport through flexible membrane liners (FMLs). They address definition of the "de minimis" contaminant transport rate. In addition, they structure technical guidance for determining whether liners are functioning properly.

Thomas R. Hauser, Director
Hazardous Waste Engineering
Research Laboratory

PREFACE

Polymeric liners are extensively used to secure pollutants in landfills, impoundments, and waste units. So that liners may be properly employed, there is need to provide technical considerations for assessing their performance. In this study, the considerations relate to pollutant transport by liners. Other considerations regarding liner environmental stress cracking, flaw formation during liner manufacturing, and liner seaming by hot melt techniques were set forth in previous reports.

We sought to provide technical considerations readily applicable to assess pollutant transport by polymeric liners. Nevertheless, technical considerations would be without meaning if they cannot foretell events with a high probability of success. Due to the scarcity of data for liners, the merit of such considerations would lie in their ability to predict the results of studies and the nature of concepts provided in the technical literature concerning material transport through polymeric materials. The usefulness of these considerations was substantiated in view of the numerous studies referenced in this work. Therewith, polymeric liner performance may be predicted.

Terms used are applicable to real-life conditions in liner service rather than their use in academic interpretations. Thus, "nonelectrolytes" (organic fluids) are defined as compounds that do not bear an electrical charge in aqueous solution (and, as concern liner service, organic fluids are the prevalent materials) rather than compounds that resist passage of electricity. There are exceptions to the definition because some organic fluids conduct electricity due to charge formation in aqueous solution. "Electrolytes" (salts) are defined as compounds that bear electrical charge

in aqueous solution, and salts are the prevalent materials because of their electrically charged constituents of matter. "Purge" relates mainly to voiding organic fluid present in the liner material and "permselective" to the selective transport of pollutants by liners due to the permeation mechanism.

We emphasized the use of metric units in conformance to preferred practice. Some deviation from metric units was necessary, however, to leave intact published data and to employ empirical methods derived using English units. "Metric Conversion Factors" precede the text to facilitate conversion to metric units.

ABSTRACT

The transport of fluids through polymeric liners used to confine pollutants in landfills and impoundments must be assessed; this report provides a technical basis for such an assessment.

When a mixture of organic fluids, water, salts, and other substances are confined by an intact liner, first the organic fluids permeate according to their mobilities, then water. Salts and also macromolecules and microorganisms remain confined. These phenomena indicate that fluids are transported by the permeation mechanism and that properly selected and installed liners made with commodity resins can be effective. Organic fluids can be one of the major factors in determining de minimis values. These permeation rates can be appreciable; therefore, impoundments with organic fluids must be selectively designed so that adequate protection of health and the environment is maintained.

The fluid mixture passes unchanged through flaws in liners. Capillary-size apertures constituting only 5×10^{-6} percent of the liner area will pass fluids at a rate equivalent to the rate of water permeation through polyethylene (assuming a free-draining subbase). The containment performance of flawed polymeric liners is obviously less than that of unflawed liners.

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ABBREVIATIONS AND SYMBOLS

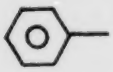
A	--	effective area
a	--	cross-sectional area of flaw
ASTM	--	American Society for Testing and Materials
^{o}C	--	degrees Celsius
C_f	--	correction factor
cm	--	centimeter
cm^3	--	centimeters cubed
CPE	--	chlorinated polyethylene
C_{PE}	--	crystallinity of polyethylene
CSPE	--	chlorosulfonated polyethylene
D	--	diffusivity
d	--	diameter
DOT	--	Department of Transportation
ECO	--	epichlorohydrin rubber
ELPO	--	elasticized polyolefin
E_p	--	apparent permeation energy
EPDM	--	ethylene propylene rubber
^{o}F	--	degrees Fahrenheit
FML	--	flexible membrane liner (polymeric liner)
$F_{m/o}$	--	flux rate of m-xylene/flux rate of o-xylene
$F_{p/m}$	--	flux rate of p-xylene/flux rate of m-xylene
$F_{p/o}$	--	flux rate of p-xylene/flux rate of o-xylene
Ft	--	foot
Ft^3	--	feet cubed
G	--	gravitational acceleration, 981 cm/sec^2
g	--	grams
gal	--	gallon
HDPE	--	high density polyethylene

hr	--	hour
I	--	Permachor
i	--	Permachor value
in	--	inch
in^2	--	inches squared
K	--	K-factor
kg	--	kilogram
L	--	average thickness
l	--	capillary length which is equivalent to membrane thickness
LDPE	--	low density polyethylene
lit	--	liter
LLDPE	--	linear low density polyethylene
M	--	slope of line
m	--	meter
m^2	--	meters squared
mil	--	one thousandth of an inch (0.001 in)
mm	--	millimeter
mm^2	--	millimeters squared
mm^3	--	millimeters cubed
mol	--	moles
n	--	viscosity
NBS	--	National Bureau of Standards
N_{Re}	--	Reynold's Number
P	--	permeation rate
$\overline{P}$	--	average permeation rate
p1-p2	--	pressure difference across membrane
Pa	--	Pascal
PB	--	polybutylene
PCTFE	--	polyethylene-co-chlorotrifluoroethylene
PE	--	polyethylene
PEEL	--	polyester elastomer
P_f	--	permeability factor

pH	--	$-\log[H_3O^+]$
phr	--	parts per hundred weight of resin
PL	--	Public Law
P_o	--	pre-exponential factor
psi	--	pounds per square inch
PTFE	--	polytetrafluoroethylene
PVC	--	polyvinyl chloride
PVDC	--	polyvinylidine dichloride
Q	--	volumetric flow rate
Q_t	--	mass per unit time
RH	--	relative humidity
R_o	--	universal gas constant
RO	--	reverse osmosis
S	--	solubility
sec	--	second
sec^2	--	seconds squared
std	--	standard
STP	--	standard temperature and pressure
SVT	--	solvent vapor transmission rate
T	--	temperature
1/T	--	inverse temperature
t	--	time
TCE	--	trichloroethylene
U	--	density
U_{PE}	--	density of polyethylene
$\overline{v}$	--	velocity of fluid
WVT	--	water vapor transmission rate
z	--	hydraulic head

Chemical Symbols:

C	--	carbon
-Cl	--	chloride
-Br	--	bromide
-S-	--	sulfur
R-	--	unspecified portion of molecule
NO_2-	--	nitrate
H_2	--	hydrogen gas
N_2	--	nitrogen gas
CO_2	--	carbon dioxide gas
CH_3-	--	methyl group
R-O-R	--	ether
	--	ester
	--	ketone
	--	aldehyde
	--	anhydride
	--	amide
$R-NH_2$	--	amine
-R-OH	--	alcohol
	--	organic acid

 -- phenyl group

-- alicyclic groups

m- -- meta position on ring

o- -- ortho position on ring

p- -- para position on ring

METRIC CONVERSION FACTORS

English system	Metric system
Angstrom	$1x10^{-10}$m
Mil (0.001 inch)	0.00254 cm
Inch	2.54 cm
Foot	30.48 cm
Yard	0.914 m
Mile (1,760 yd)	1.609 km
Square inch	6.452 cm^2
Square foot	0.092 m^2
Square yard	0.836 m^2
Cubic inch	16.387 cm^3
Cubic foot (1,728 in^3)	0.028 m^3
Cubic yard (27 ft^3)	0.7646 m^3
Pound (Mass)	
avdp. (16 oz)	453.592 g
troy (12 oz)	373.24 g
Gallon (U.S., 4 quarts)	3.785 liters
Ton	
long (2,240 lb)	1.016 t
short (2,000 lb)	0.907 t
Pounds (Force) per square inch	$6.895x10^4$
1 gal/acre·day	0.935 g/m^2·day

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Our thanks to Miss Annabelle Cortez for technical support. She conducted the extensive library research required for this study.

SECTION 1
INTRODUCTION

Polymeric lined landfills and impoundments are regulated under RCRA and associated background and guidance documents. Pursuant to Section 3004[0] and 3015 of the Hazardous and Solid Waste Amendments of 1984[1] and minimum guidance technology for double-liner systems,[2] polymeric liners must prevent migration of constituents of the waste liquid into the liner during the period the unit remains in operation (including any post-closure monitoring period) except for de minimis leakage. EPA recognizes that polymeric liners will not always have zero leakage and that de minimis leakage may occur. De minimis leakage can occur as a result of vapor passing through the liner, very small imperfections in the liner that occur very rarely, or a seam that has a very small crack or hole.

This report sets forth technical considerations regarding de minimis transport rates for polymeric liners and guidance for assessing liner performance, based on extensive review of the technical literature. The literature searching techniques in this study are given in Appendix A.

EPA believes that current state-of-the-art technology for FML installation allows for hazardous waste management units to be built that will have very low leakage rates at installation. EPA does not have a specific maximum de minimis leakage rate that can be recommended. However, based on currently available preliminary field data, laboratory test results, and professional judgment, EPA believes that de minimis leakage should be approximately 1 gallon/acre/day or less. This rate should not be taken as a hard and fast rule because there are conditions where vapor transmission potentially could exceed this value. Also, this value does not apply to organic liquids, many of which can permeate an FML independently of the water in waste liquid.

The purpose of this study is to assess the transport of pollutants through polymeric liners employed in hazardous waste landfills and impoundments. Its objectives are: (1) to set forth technical considerations for assigning "de minimis" passage rates for pollutants in RCRA regulations or background documents, and (2) to provide guidance for assessing serviceability of liners with regard to regulations.

In a previous study, de minimis is set forth as a bench mark for specifying acceptable performance for liners -- allowable rate of passage of effluent material. This rate is related to water transport rate by permeation of chemically modified polyethylene liners. Material transport at rates greater than 1 gal/acre day indicates liners are functioning improperly. Guidelines are based on properties of liners such as swelling and mechanical strength loss associated with their soaking in leachate. These are set forth as simple and convenient methods for determining whether liners function properly under service conditions. Exceeding specified limits in property values is interpreted to mean that material transport is occurring at rates greater than that allowable, thus inferring liners are not functioning within design specifications.

Polymeric liners were assessed for their ability to contain water, nonelectrolytes (organic fluids), and electrolytes (salts). Water transport rate was found to be an improper indicator for estimating passage by permeation because the correlation between rates for water passage and pollutant passage is unsubstantiated. Water, not being a pollutant and an improper indicator for gauging pollutant passage, should therefore be discontinued in defining de minimis. Nonelectrolytes and electrolytes differ appreciably with regard to their abilities to permeate polymeric materials. Generally, polymeric membranes are not high performance barriers against organic fluids. By contrast, permeation of membranes by electrolytes is an improbable occurrence and other material such as macromolecules and microorganisms are similarly securely confined.

Rather than basing de minimis on rate of water passage, de minimis should be based on rate of passage of nonelectrolytic pollutants (organic fluids) by permeation. The rate may be appreciable even though it is the minimum value with regard to passage mechanisms. From a practical point of view, the rate of effluent formation should not exceed the capability to manage it at the disposal site. In general, electrolytes are expected (as indicated above) to be securely confined by liners in the absence of apertures. Thus, the de minimis passage rate for electrolytic pollutants such as heavy metal salts is "nil," i.e., within applicable effluent limitations and standards regarding groundwater protection as specified in PL 98-616, Section 215(10). Organic fluids are the fugitive pollutants (i.e., material transported across the polymeric element of the liner system) of polymeric lined landfills and impoundments. Their rates of passage are most accurately determined from experimental data; yet in the absence of such data, their rates may be estimated by employing the Permachor Method with respect to polyethylene liners.

Liner serviceability guidelines should be based on permselectivity properties of liners. A liner is deemed to be functioning improperly when salts are not effectively confined. Another useful indicator of liner unsuitability is passage of organic fluids in tandem with water. A waste containing water, salt, and organic fluids confined by flawless polymeric liners (i.e., liners free of holes, apertures, and tears) is expected ideally to issue first organic fluids, then water, but not salt.

Liner performance is assessed by its ability to confine salt. This ability of liners to confine salt confirms their proper functioning, i.e., allowing only vapors/liquids to permeate by the permeation mechanism. Polymeric liners are expected to hold salt when solvated by organic fluids; the literature indicates resins to be impermeable by salts even when swollen by organic fluids to gel-like consistencies. However, more substantiation of liners retaining salts even when swollen is desirable for liner

compositions. Passing of salt may indicate apertures in liners due to their weakened state from organic fluid plasticization. Changes occurring in permeation rates for vapors/liquids in polymeric liners capable of retaining salt indicate changes in their polymer morphologies. Such rate changes may occur upon discharge of the nonelectrolytic portion of the confined pollutants. Nevertheless even with morphological changes, it is assessed that vapors/liquids passage rates would be similar to those determined for virgin material, with liners formulated with plasticizer being a probable exception to this generalization.

Salt in fugitive materials (and in addition macromolecules and microorganisms) in concentrations exceeding nil amounts would indicate flaws in liners. In such cases, vapors/liquids passage rates would exceed de minimis rates because loss of material would occur through apertures in addition to that lost by permeation. This study shows polyethylene liners with capillary-size apertures constituting only 5×10^{-6} percent of the liner area would transport fluid at a rate equivalent to that for water permeation. This transport rate estimate assumes a free draining subbase; in practice, however, liquid flow may be attenuated because this is generally not the case. Obviously, flaws significantly depreciate the barrier performance of polymeric liners.

SECTION 2
RECOMMENDATIONS

Users of polymeric liners employed to contain toxic wastes in landfills and impoundments need guidance to monitor the serviceability of the liners. The guidance is needed to assess whether liners perform according to regulations regarding liners for pollutant control. EPA should incorporate such guidance into RCRA hazardous wastes regulations or related background and guidance documents. The regulations should underscore "de minimis," which specifies the allowable rate of transport of pollutants by liners. Rates exceeding those fixed by de minimis would indicate liner noncompliance to regulations whereas lesser ones presage regulatory compliance.

Regulations concerning polymeric liners should employ technical considerations of material transport phenomena. Because of lack of information about liners, the pertinent field of technology for literature investigation concerns polymeric membranes. Reverse osmosis (RO) membranes show features that should be of commonality with those of polymeric liners. An important one is their impermeability to salt essentially notwithstanding the hydrostatic pressures of aqueous salt solutions. Polymeric liners have compositions that should also exhibit this feature. Whereas advanced RO membranes yield the greatest amount of water flux, liners need not be geared to minimal water transport for effective salt pollutant control.

The effectiveness of polymeric liners as barriers to pollutant migration is manifested essentially without regard to their permeable nature by water. This assessment is futher substantiated because polymeric materials, generally, are impermeable by salts even when saturated by water. Heavy metal salts and organic salts exemplify that flawless polymeric liners

should effectively control. Similarly, this assessment applies to macromolecular contaminants and microorganisms. However, polymeric materials are permeable by organic fluids. The major disadvantage of polymeric liners as barrier materials concerns control of these fluids. But the degree of control cannot be estimated by their susceptibility to water permeation.

The literature indicates organic fluid transport by permeation of polymeric membranes is not coupled to water transport. Polymeric membranes holding water and dissolved low molecular weight nonelectrolytes (organic fluids) transport nonelectrolytes to the exclusion of water. For organic fluid in water, transport rates are lower than transport rates of pure fluids, but rates remain in the same relative order for their fugacities. Water transport occurs when the organic fluid portion of the mixture is purged (voided) by the membrane. Regarding permeation of polyethylene membranes by organic fluids, the Permachor approach is employable to calculate their transport rates. But literature sources are not explicit whether permeation rates of polymeric materials by mixtures of nonelectrolytes in water occur at rates equivalent to those obtained by summing their respective rates of permeation.

State-of-the-art polymeric liners functioning ideally are viewed to permeate organic fluids before permeating water and to hold salt. Their passage rates should not exceed those due to transport by permeation. These rates relate to the nature of the polymeric materials and penetrants. Following the classical division of materials into electrolytic and nonelectrolytic ones, de minimis should specify transport rates for individual nonelectrolytes but assign nil transport rates for all electrolytes. If, however, the accumulation of organic fluids exceeds the pollutant management capacity at the waste enclosure site, the permeability rates for organic fluids may not be tolerable.

Guidance for assessing liners regarding ideal service should address monitoring the amount of salt in the fugitive material; and the transport

rate for organic fluids should not exceed that from permeation. No concurrent transport of organic fluids and water should occur. Allowance should be made in these strictures for real-life liners and service conditions by conforming them to effluent waste limitations.

The presence of salt in fugitive material indicates flaws in polymeric liners. This study considers flaws as circular apertures and categorizes them as capillaries and larger holes. Given the nature of the apertures, their prevalence in the liner may be estimated from salt flux determinations.

Commercially available polymeric liners are fabricated from commodity resins that exhibit useful properties for pollutant control such as impermeability by salts and other materials. As a result, liners in service should be required to perform accordingly. For electrolytic contaminants, de minimis should be nil. For practical purposes, the amount should not exceed salt limitations relating to groundwater protection [PL 98-616; Section 215(10)]. Furthermore, de minimis should specify that liner systems retain macromolecules and microorganisms as well as salts.

Despite their impermeability by electrolytes, commodity resins are permeable by nonelectrolytes (organic fluids). De minimis should quantify allowable transport of nonelectrolytic pollutants according to their permeabilities. This will be needed for each type of polymeric liner employed. Organic fluid types and their concentrations in the waste consignment should be considered; provision should then be made at the disposal site so that the consignment's effluent does not exceed amounts given in de minimus specifications.

Emerging technologies in polymer synthesis should be monitored to identify materials that would reduce the rate of transport for organic fluids. Recent developments in packaging, container and resin technologies provide basic technology useful for advancing future liner performance,

e.g., HDPE/nylon high barrier resins. Their use would lessen the impact of organic fluids in newly formed landfills and impoundments. But in this respect, engineering judgment should balance the benefit of managing organic fluids at a reduced rate of transport versus managing at a higher rate. The latter may be better because of earlier purging of organic fluids.

Liner serviceability guidance should be based on comparative chemical analyses of fugitive material and the confined waste. Of particular significance would be salt, organic fluids, and water determinations. Salt in the effluent would indicate liner holes may be present; its concentration and flow rate may be used to calculate amounts of effluent resulting from liquid passage through liner holes. Another indication of flaws would be organic fluid and water issuing jointly; the extent of water dilution of organic fluids may also be employed to assess the amount of fluid flow stemming from holes/flaws in liners.

SECTION 3
TECHNICAL DISCUSSION

Hazardous wastes can be transported through polymeric liners by flow through flaws (holes) and by permeation. The transport mechanisms will affect the compositions of the fugitive materials versus that of the confined fluids. Fluids passing through liner holes will not change their composition. Fluids permeating a polymeric liner will undergo compositional changes to the extent that fugitive materials will be free of electrolytes (salts). This will not be the case for nonelectrolytes (organic fluids) however. Thus, the effectiveness of liners to control pollutants cannot be estimated by their degree of water permeability.

Rather than water, the permeabilities of organic fluids should be addressed. Their permeabilities are determined by the following equation:[3-5]

$$P = DS \qquad (I)$$

where P = permeability coefficient
D = diffusivity of penetrant in liner
S = solubility of penetrant in liner

To simplify permeability estimates, we searched the literature to see if permeability can be estimated by considering only the solubility term of equation I. Permeability was found not predictable by employing only solubility values; but rough correlations were shown, in a few cases, with diffusivity.[6] The diffusivity term of equation I, however, is more difficult to determine than is solubility. For estimating permeability of

polyethylene (PE) by organic fluids using tabulated information, the Permachor approach was described and the literature exhibits its usefulness. This empirical approach and examples of its use are given under "Permachor Method."

Despite the lack of suitability of solubility to predict permeability in equation I, the impermeable character of polymeric liners can, nevertheless, be anticipated when solubility diminishes to zero (except for highly diffusive penetrants such as hydrogen gas). To estimate probable impermeability, the use of solubility parameters may be considered when assigning high barrier properties to liners for pollutants. On this basis, we estimate flawless polymeric liners to be essentially impermeable to electrolytes. The literature gives experimental evidence to substantiate their insoluble nature.[7,8] The passage of electrolytes by flawless liners should be nil essentially notwithstanding the hydrostatic pressure head of their aqueous solution. This phenomenon forms one basis for assessing performance of reverse osmosis (RO) membranes.[9-11]

It is appropriate to compare flawless polymeric liners to RO membranes. Manufacturing processes for liners and RO membranes share a similar objective, differing mainly with respect to maximizing water flux with RO membranes. As indicated earlier, this is not important for evaluating liners. The objective of manufacturing liners differs from those for the microporous membranes used for microfiltration,[12-16] dialysis,[17] and ultrafiltration.[18-22] Using such materials as liners would be inappropriate for landfill service because they may pass pollutants such as electrolytes, macromolecules, and microorganisms. For applications that indeed tolerate or require the passage of electrolytes and retention of selected species, manufacturing procedures for realizing appropriate materials are structured accordingly. Such procedures are those to be circumvented in liner manufacturing.

We noted a lack of information concerning permeation by electrolytes

through polymeric materials solvated by organic fluids. On the basis of solubility parameters, by weighted averaging, solvated liners were estimated to be essentially impermeable to electrolytes. Although organic substances per se may exhibit some propensity for dissolving electrolytes, this property may not manifest itself within the liners. The literature gives experimental evidence to support this assessment. For example, permeation through PE by various alcohols, amines, esters, aldehydes, and ketones at various pH values showed transport of only the unionized organic species; organic electrolytes were excluded from permeating the PE.[6] Despite the importance of swelling phenomena regarding mechanical properties of polymers, liner permeation by electrolytes is essentially unaffected by plastization of the liner by organic fluids.[8,23] Liquids and polymeric gels, having virtually zero mechanical strength, have been employed as effective diffusion barriers and separation media, e.g., solar gel ponds,[24] liquid membranes,[25,26] immobilized liquid membranes,[27] and gels for electrophoresis.[28] Thus, liner swelling data per se is not appropriate for estimating liner permeability by electrolytic pollutants.

For semi-crystalline polymers, solvation by organic fluids occurs mainly in the amorphous phase of polymers. Liners fabricated from semi-crystalline polymers are assessed to be permeable according to their amorphous fraction. Thus, greater liner crystallinity increases liner resistance to permeability by organic fluids. In this respect, comparison of high density polyethylenes (HDPE) which have only small differences in densities shows significant differences in their values for permeation rates.[29]

Figure 1 illustrates the general relationship of the permeation rate of an organic liquid (benzene) to polyethylenes of various densities. Notice that small reductions in densities result in PE films with higher permeabilities, particularly below 0.93 g/cm^3. This relationship can be understood on the basis of PE crystallinity. The greater densities signify higher degrees of crystallinity. Approximation of the fractional degree of

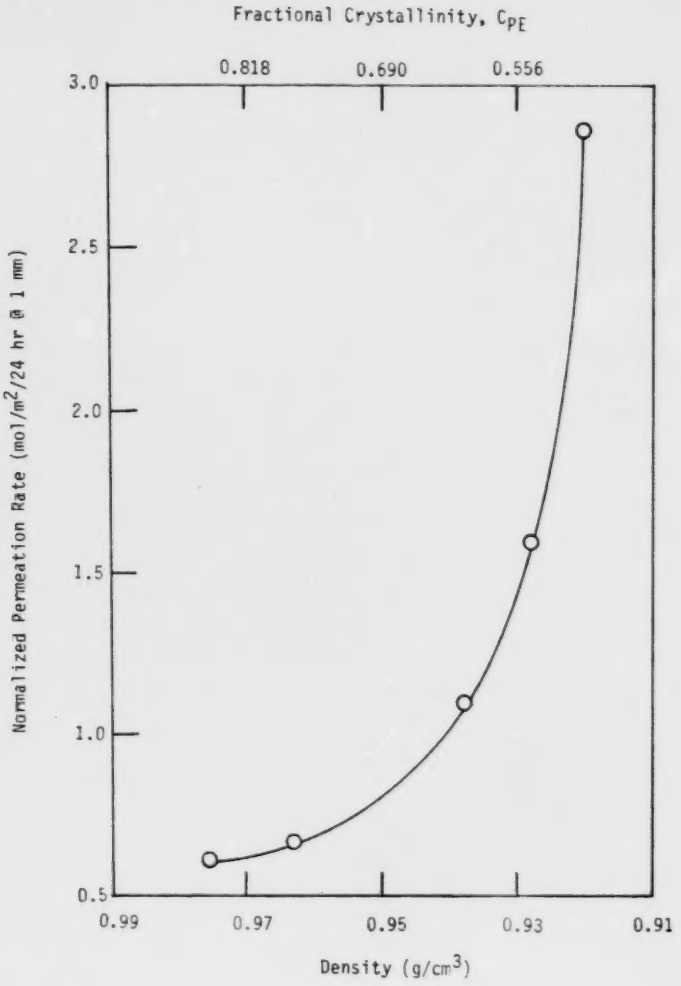

Figure 1. Permeation rates of benzene as a function of polyethylene density and crystallinity

C_{PE} was calculated from a method employed by Chiu, et. al.

(adopted from references 29 and 30)

crystallinity, C_{PE}, from PE density, U_{PE}, follows from the Chiang/Flory relationship:[30]

$$0.145\ C_{PE} = 1-(0.855/U_{PE}) \qquad \text{(II)}$$

Although density changes have a pronounced effect on polymer crystallinity and permeability (Figure 1), the effects on permeability from morphological characteristics such as spherulite size, orientation of spherulites, and diffusion paths are not apparent.

The above information indicates use of PE and other resins with higher degrees of crystallinities would yield liners with greater resistance to permeation by organic fluids. This benefit, however, may be mitigated by other considerations. For example, HDPE liners made with PE resins having densities at or below about 0.94 g/cm^3 are reported to have superior performance in environmental stress-cracking tests given in NSF 54.[31]*

The passage of electrolytic substances through liners indicates transport mechanisms other than permeability are operating. In contrast with permeability, the compositions of fugitive materials stemming from holes in liners will reflect those of the fluid confined by the liner in the vicinity of the holes. When this occurs, the liner essentially loses its permselective nature even though permeability mechanisms are still operating because the volume passing through holes is significantly greater than the volume permeating the liner. This is illustrated in subsequent subsections under "Flow Through Small Flaws" and "Flow Through Large Flaws."

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* Personal communications with J.D. Vandervoort, Technical Director of Schlegel Lining Technology, Inc., 6/10/85, and with D. Eakin, President of Gundle Lining System, Inc., 6/11/85.

In this report, calculations carried out concerning waste passage through holes assume holes are of uniform bore and parallel. Liquid is assumed to free drain through such holes. Differentiating holes as to how they affect liquid flow are the ratios of hole diameters to lengths and to aperture edge effects. Parameters due to wall effects and to the edge effects of holes on liquid flow are significant when determining flow through small and through large diameter holes, respectively.

In subsequent calculations under "Flow Through Liner Flaws," we estimated the amount of fugitive material per day stemming from one acre liners by assuming different mechanisms for material transport. Contaminant transport may be separated into three categories: (1) permeation, (2) capillary (small hole) flow, and (3) large hole flow. In this study, we have addressed each category.

Permeation is the predominant transport mechanism operating in flawless polymeric materials. Gases and vapors are preferentially transported in a three-step process (i.e., adsorption, molecular diffusion or Knudsen flow, and desorption). Often, the permeability coefficient for a given polymer/penetrant system is expressed as follows:[5]

$$P = Q_t L/[A(p1-p2)] \qquad \text{(III)}$$

where Q_t = mass per unit time the material has permeated through the membrane

L = average thickness

A = effective area

$p1 - p2$ = pressure difference across the membrane

Gas and vapor transmission rates can be computed from tabulated permeability coefficients.[32]

In membranes having large enough holes, transport may be regarded as

flow of incompressible fluid through uniform cylindrical holes normal to the membrane's surface. In this report, we have modeled such capillary flow using the Hagen-Poiseuille equation:[3,33]

$$Q = (UGzd^4)/(128nl) \qquad \text{(IV)}$$

where Q = volumetric flow rate
U = fluid's density
G = gravitational acceleration, 981 cm/sec^2
z = hydraulic head
d = hole (capillary) diameter
n = fluid's viscosity
l = capillary length which is equivalent to membrane thickness

Rationale for using equation IV stems from the following considerations: (a) because liners with holes are assumed to filter particles in a manner analogous to porous/microfiltration membranes, the range of operating data for porous/microfiltration membranes (i.e., pressures and minimal particle size separation criteria) suggests particles down to 5 x 10^{-6} cm (500 Angstroms) could be separated by liners subjected to hydrostatic pressures in the range of 3.45 x 10^5 - 3.45 x 10^6 dynes/cm^2 (5-50 psi),[9,34-37] (b) a maximum applicable Reynold's number (N_{Re}) of 580[3] reported by Barrer, (c) the maximum hydrostatic pressure head of 1.93 x 10^6 dynes/cm^2 (28 psi) anticipated for deep 914 cm (30 ft) surface impoundments,[38] and (d) an assumed average liner thickness of 0.2032 cm (80 mil). From these considerations, a rough applicable range for the hole (capillary) diameter in equation IV is:

$$5 \times 10^{-6} \text{ cm} < \text{hole diameter(d)} < \text{about } 0.012 \text{ cm } (\sim 5 \text{ mils})$$

Thus, for discussion purposes in this report, we presumed that pollutants permeate through liners having holes with diameters below ~ 5 x 10^{-6} cm. Leakage through 0.2032 cm (80 mil) liners having holes greater than 0.012 cm

(- 5 mils) may be presumed to be characterized by other flow types such as the Chezy flow.[33] (Calculations relating N_{Re} and the Hagen-Poiseuille equation are given under the subsection "The Relationship Between the Poiseuille and Bernoulli Equations.") In our literature survey, we determined that little practical information was available concerning the estimation of flow in liners within transition regions between permeation/capillary flow or capillary/Chezy flow. Work related to the latter is underway at Texas A&M.[39]

LINER PERMEABILITY

Polymeric liners were initially used to control the transmission of water and trace metals to groundwater. "To these species polymeric membranes have shown extremely low permeation."[8] In this respect, liners resist migration of electrolytes in a manner analogous to RO membranes. Nevertheless, RO and liner type polymeric materials are well known to be permeable to organic species.[40,41]

In general, liners in current use exhibit permselective properties, i.e., they are permeable by certain species but to different extents for each molecular specie under a given driving force. This property forms the basis for membrane separation processes based on hyperfiltration[42,43] and pervaporation.[44] The following examples illustrate the permselective nature of liner-type materials.

One example of permselective properties of 1.0 mm (40 mil) thick HDPE is given in Table 1. In this study by August and Tatzky, permeation rates were measured for each component of an equal volume mixture of six solvents. The relative differences in permeation rates for components in the mixture reflect the same ranking in rates for pure solvents. A second example of permselectivity of PE was reported by Michaels and co-workers at MIT.[45] PE air-blown films were shown to be capable of separating isomers of xylene.

TABLE 1. PERMEATION RATES OF A MIXTURE OF HYDROCARBONS THROUGH HDPE

(adopted from reference 40)

Hydrocarbon	Permeation Rate $g/m^2 \cdot day$
Trichloroethylene	9.4
Tetrachloroethylene	8.1
Xylene	3
iso-octane	0.8
Acetone	1.4
Methanol	0.7
Total Hydrocarbons	23.4

Preconditioning films by soaking in a specific isomer enhanced permselectivity for a given isomer. Table 2 summarizes the effects of preconditioning (i.e., soaking PE in p-xylene and annealing at elevated temperatures) on the permselectivity for separate isomers. Although liners are not preconditioned for such purposes, the example shows the permselective nature of PE toward even closely related organic species.

Permachor Method

Numerous attempts to quantify permeability using solubility or diffusivity data of penetrants in polymers, or upon various properties of penetrants have been largely unsuccessful.[5,23] Some qualitative

TABLE 2. EFFECTS OF XYLENE ISOMER SORPTION ON PERMEABILITY AND PERMSELECTIVITY
(adopted from reference 45)

Permeant	Conditioning Temperature, °C	Average Permeability Coefficient, 10^5(b)	Permselectivity(a) $F_{p/o}$	$F_{p/m}$	$F_{m/o}$
Low-Density Polyethylene(c) at Permeation Temperature of 40°C					
o-Xylene	Unconditioned	19.4			
m-Xylene	Unconditioned	22.4	1.35	1.17	1.15
p-Xylene	Unconditioned	26.2			
o-Xylene	50	26.1			
m-Xylene	50	29.1	1.39	1.25	1.12
p-Xylene	50	36.3			
o-Xylene	55	31.1			
m-Xylene	55	34.4	1.25	1.15	1.10
p-Xylene	55	38.8			
High-Density Polyethylene(d) at Permeation Temperature of 30°C					
o-Xylene	Unconditioned	1.81			
m-Xylene	Unconditioned	2.12	1.62	1.39	1.17
p-Xylene	Unconditioned	2.94			
o-Xylene	95	17.1			
m-Xylene	95	16.6	1.20	1.23	0.97
p-Xylene	95	20.5			
o-Xylene	100	18.2			
m-Xylene	100	24.8	1.62	1.18	1.36
p-Xylene	100	29.3			

(a) Permselectivity expressed as ratios of flux rates:
$F_{p/o}$ = flux rate of p-xylene/flux rate of o-xylene
$F_{p/m}$ = flux rate of p-xylene/flux rate of m-xylene
$F_{m/o}$ = flux rate of m-xylene/flux rate of o-xylene
(b) $(g \cdot cm)/(cm^2 \cdot hr \cdot cm\ Hg)$.
(c) Films conditioned in liquid p-xylene, cooled, and dried at 0°C.
(d) Films conditioned in p-xylene, cooled, and dried at 25°C.

relationships have been reported as shown in Table 3. In general, the permeability of a given penetrant in a polymer is derived from transmission or sorption-desorption experimental data.[41] Such experiments require exacting experimental conditions. Nevertheless, for polyethylene and polypropylene, a simplified empirical method has been developed to estimate the permeabilities of organic species. The Permachor Method provides the means to mathematically estimate the permeabilities of organic species through polyethylene and polypropylene based on "Permachors."[6] The method is discussed below.

The transport of nonelectrolytic contaminants through flawless polymeric liners may be most accurately predicted from applicable, experimentally derived permeation rates. A large body of published information is available concerning permeation of polymers. Investigators report "permeabilities" having a wide range of units. Tables B-1 through B-16 of Appendix B provide a few examples of published data on liner polymers and similar materials. Thus, care must be exercised when employing such data. (Some studies show that permeability rates are slightly higher if measured for pure organic liquids in contact with PE than those rates measured for PE in contact with their saturated vapors.[45] However, this difference did not appear to be significant in liner applications.) The essential features of the method have been verified by the National Bureau of Standards and Department of Transportation for use in predicting permeability through PE.[29] Permeabilities of organic liquids are predictable at various temperatures[6] and for various types of PE.[29] A review of the method and examples of its use are given below.

Equation I expresses the permeability coefficient as a function of diffusivity and solubility. Alternatively, equation V shows that the permeability coefficient for a given penetrant/polymer system can also be expressed as a function of the "apparent permeation energy," E_p, at temperature, T, in a form analogous to the Arrhenius equation, where R_0 and and P_0 are the universal gas constant and pre-exponential factor,

TABLE 3. EFFECTS OF BARRIER AND PENETRANT PROPERTIES ON PERMEABILITY

Properties			Effects of Increase in Property on	
Penetrant	Organic Semicrystalline Polymers	Polymer Studied	Permeability	Reference
Molecular weight	-	PE	reduction	5
-	grafting	PE	increase	46
Size	-	-	reduction	4
Shape	-	-	reduction	4,45
Temperature	temperature	PE	increase	29
-	crystallinity	PTFE	reduction	23
-	path tortuosity	polybutadiene	reduction	47
-	density	PE	reduction	29
-	crystallite morphology	PE	various	48
-	preconditioning with penetrant	PE	enhanced permselectivity	45
Polarity	-	PE	reduction	39
-	free volume		increase	49
-	plasticizers	PVC	increase	50
-	biaxial mechanical orientation	PE PTFE	slight reduction	51
liquid state (vs. saturated vapor)	-	PE	slight increase	45
solubility parameter close to PE parameter	-	PE	reduction penetration lag time	52
concentration (in dilute solution)	-	PE	increase	53

respectively.

$$P = P_0 \exp[-E_p/(R_0T)] \qquad (V)$$

Equation V may be written in the following logarithmic form:

$$\ln P = \ln P_0 - [E_p/(R_0T)] \qquad (VI)$$

where $\ln P = (1/2.303)\log P$

To evaluate this relationship, according to Salame, Bent used permeability data for various organic liquids in contact with PE at various temperatures to plot logarithms of P versus (1/T), absolute temperature. The resulting plot for each penetrant yielded a straight line having a constant slope of $(-E_p/R_0)$.[6] By extrapolating the line where (1/T) equals 0, the value of P_0 was obtained from equation VI.

Permachor Values--

Attempts by Salame to correlate permeability with a single penetrant property such as size, shape or polarity were unsuccessful.[6] For homologs of straight-chain hydrocarbons, however, it was found that semilog plots of P_f, defined as a permeability coefficient versus the number of carbon atoms in each molecule yielded a linear relationship. Moreover, studies of other families of organic compounds (e.g., alkenes, alcohols, ketones) produced similar linear graphs, but they were displaced by characteristic factors relative to the graph for straight-chain hydrocarbons. By assigning unity for the ordinate value for one carbon atom and normalizing other categories of compounds according to the results from straight-chain hydrocarbon studies, Permachor values, i, were developed by Salame for atoms or chemical groups present in compounds studied. These values are given in Table 4. The Permachor (I) for a particular compound is derived by simply adding the

TABLE 4. PERMACHOR VALUES, i, FOR ATOM OR GROUP TO BE USED IN ESTIMATING P_f BY EQUATION VI
(adopted from reference 6)

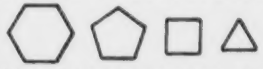
Atom or Group	Number of Carbon Atoms in Molecule										
	1	2	3	4	5	6	7	8	9	10	>10
Acid (--C(=O)-OH) Aliphatic	18.0	13.5	13.5	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0
Acid (--C(=O)-OH) Aromatic	--	--	--	--	--	14.0	14.0	14.0	14.0	14.0	14.0
Alcohol (--OH) Aliphatic	16.5	16.5	15.5	14.0	14.0	11.0	11.0	10.0	10.0	10.0	10.0
Alcohol (--OH) Aromatic	--	--	--	--	--	13.0	13.0	13.0	13.0	13.0	13.0
Aldehyde (R-C(=O)-H)	17.8	12.0	12.0	9.5	9.5	8.0	8.0	8.0	8.0	8.0	8.0
Alicyclic 	Add 1.0 below 80°, 2.0 above 80°F										
Amide (--C(=O)-N-)	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0
Amine ($--NH_2$) Aliphatic	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Amine ($--NH_2$) Aromatic	--	--	--	--	--	11.0	11.0	11.0	11.0	11.0	11.0

TABLE 4. (CONTINUED)

Atom or Group	Number of Carbon Atoms in Molecule										
	1	2	3	4	5	6	7	8	9	10	>10
Anhydride (-C(=O)-O-C(=O)-)	--	15.8	15.8	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0
Bromine (--Br)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Carbon (--C--)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.93
Chlorine (--Cl)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Double Bond Between Carbons	Subtract 0.2										
Ester (-C(=O)-O-)	--	9.6	9.6	8.0	7.0	7.0	7.0	3.1	3.1	3.1	3.1
Ether (R-O-R)	--	2.4	2.4	2.4	2.4	1.4	1.4	1.4	1.4	1.4	1.4
Iso - substitution & side branching	Add 2.0										

TABLE 4. (CONTINUED)

Atom or Group	Number of Carbon Atoms in Molecule										
	1	2	3	4	5	6	7	8	9	10	>10
Ketone (R-C(=O)-R)	--	10.8	10.8	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5
Nitrate ($--NO_2$)	15.4	13.4	13.4	13.4	13.4	9.6	9.6	9.6	9.6	9.6	9.6
Phenyl(⬡) Benzene	--	--	--	--	--	5.4 below 80^{o}, 7.6 above 80^{o}F					
Mono,ortho & meta	--	--	--	--	--	5.4	5.4	5.4	5.4	5.4	5.4
Para	--	--	--	--	--	3.8 below 80^{o}, 5.4 above 80^{o}F					
Sulfur (-S-)	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0

Permachor values of groups or atoms present in the compound.

The relationship between Equation I and the permeability factor, P_f, follows from convention set forth by Salame.

$$P_f \equiv DS \qquad \text{(VII)}$$

The permeability coefficient and the permeability factor differ by a proportionality constant related to the thickness of the membrane. The relationships between i, I, and P_f are described in the following section.

Permeabilities Based on Permachors--

The Permachor Method requires two equations. The first computes the Permachor from Permachor values using equation VIII, where I is the sum of the Permachor values, $i_1+i_2+\ldots i_n$, for the atoms or groups in the compound.

$$I = i_1+i_2+\ldots i_n \qquad \text{(VIII)}$$

Salame derives the general linear relationship between P_f and I for organic liquids at various temperatures in equation IX.[6]

$$\log P_f = K-(MI) \qquad \text{(IX)}$$

where K = constant termed the K-factor which is related to temperature and specific polymer type (e.g. LDPE, HDPE)

M = slope of graph related to general polymer class (e.g. polyethylene, polypropylene)

(The equation provides P_f in units of grams/24 hr/100 in^2/0.001 in thickness, which can be readily converted to the CGS system of units, gr/sec/cm^2/cm, by multiplying P_f by the following factor: 1.094×10^{-4}.) It should be noted that Permachors for compounds are computed from Permachor values listed in Table 4 without regard to grades and types of polyethylenes and polypropylenes.(6) Computation of P_f values from Permachor requires modification of equation IX: K-factors must be used for specific polymer grades (e.g., HDPE, LDPE) and M must correspond to generic polymer type (e.g., polyethylene, polypropylene). Table 5 lists a few values for K and M reported by Salame.

Table 6 provides tabulated data for 79 organic liquids showing permeabilities derived experimentally for LDPE with those calculated by use of Permachors.(6) Table 7 lists data for HDPE and polypropylene showing similar results. (Note: The same Permachors for compounds listed on Table 6 are employed in Table 7.) Table 8 describes six compounds yielding P_f values that are much less accurate than previous examples; thus care must be exercised when using Permachors under conditions similar to those of Table 8.

Examples of use of Permachors follows:

Example 1:

Methanol, CH_3OH, has a Permachor (I) and permeability factor, P_f, as follows:

Step 1: Computation of I

one carbon @	i	= 1.0
one aliphatic OH @	i	= 16.5
	I	= 17.5

Step 2: Computation of P_f using the general relationship of log P_f = K-(0.22 I) and assuming Phillips type HDPE @ 73°F, K = 3.36 (Table 5)

$$\log P_f = 3.36-(0.22\ I)$$
$$\log P_f = 3.36-[0.22(17.5)] = 0.49$$
$$P_f = 0.32 \text{ g/24 hr/100in}^2\text{/0.001 in thickness}$$

TABLE 5. SUMMARY OF SELECTED PERMACHOR EQUATION VALUES

Polymer Type	K	M
LDPE	4.17 @ 73°F 4.98 @ 120°F	0.22
HDPE:		
Ziegler-type	3.21 @ 73°F	0.22
Phillips-type	3.36 @ 73°F	0.22
All types	4.10 @ 120°F	0.22
Polypropylene	4.17 @ 73°F 4.98 @ 120°F	0.26

TABLE 6. CALCULATED AND EXPERIMENTAL PERMEABILITY FACTORS FOR ORGANIC COMPOUNDS IN REGULAR LOW DENSITY POLYETHYLENE
(adopted from reference 5)

Permeant	Permachor for Compound	P_f in g/24 hr/0.001 in^2/0.001 in							
		32°F		70°F		130°F		165°F	
		Exp.	Calc'd	Exp.	Calc'd	Exp.	Calc'd	Exp.	Calc'd
Alcohols									
Allyl alcohol	18.3	0.16	0.09	1.45	0.86	23	17	138	75
i-Amyl alcohol	21	--	0.02	0.2[a]	0.22	--	43	--	19
Benzyl alcohol	19.4	--	0.05	0.4	0.5	--	10	--	42
n-Butyl alcohol	18	0.1[a]	0.11	0.46	1.0	20.4	20	150	87
s-Butyl alcohol	18	0.12[a]	0.11	0.62	1.0	37.6	20	278	87
t-Butyl alcohol	20	0.05[a]	0.04	0.26	0.36	27	7	236	32
Diethylene-glycol	34	--	--	--	--	--	--	0.76	0.02
Ethyl alcohol	18.5	--	0.07	0.7[b]	0.76	--	15	--	67
2-Ethyl-hexanol	20	--	0.04	0.3	0.36	--	7	--	32
Ethylene glycol	30	--	0.0002	--	0.002	--	0.05	1.26	0.2
Ethylene glycol-monobutyl-ether	18	--	0.11	0.67	1.0	35	20	180	87
Furfuryl alcohol	20.6	--	0.03	0.24	0.27	--	5.2	--	23
Glycerin	49.5	--	--	--	--	0.36	--	1.6	0
Heptyl alcohol	18	--	0.11	1.0[b]	1.0	--	20	--	87
Hydroquinone	31.4	--	--	--	--	0.06	0.02	0.36	0.10
Methyl alcohol	17.5	0.25	0.14	0.22	1.3	27.8	25	100[a]	110
Octyl alcohol	18	0.10	0.11	0.5	1.0	25.6	20	188	87
Phenol	18.4	0.10[a]	0.09	0.5	0.8	24	16	120	70
n-Propyl alcohol	18.5	0.07	0.07	0.5	0.8	22.4	15	168	66

TABLE 6 (CONTINUED)

Permeant	Permachor for Compound	P_f in g/24 hr/0.001 in^2/0.001 in							
		32°F		70°F		130°F		165°F	
		Exp.	Calc'd	Exp.	Calc'd	Exp.	Calc'd	Exp.	Calc'd
Amides									
Acetanilide	25.4	--	0.002	0.02[a]	0.025	0.4	0.54	3.4	2.0
Formamide	19	--	0.065	0.5	0.6	--	12	--	52
Amines									
Aniline	16.4	0.25[a]	0.24	1.7	2.3	59.6	45	294	200
m-Chloroaniline	17.6	--	0.13	1.6	1.3	--	24	--	100
i-Propyl amine	11.0	2.3	3.8	40.8	36	700[a]	680	3200[a]	3000
Halogenated Hydrocarbons									
Carbon tetrachloride	5.8	51	54	610	500	7830	9200	45000	42000
Chlorobenzene	6.6	57.8	36	455	340	4410	6200	21150	28000
p-Chlorotoluene	6.0-7.6	30	48	304	450	4170	3800	18500	17000
1,2-Dibromo-ethane	8.0	--	17	140	160	--	3100	--	14000
o-Dichloro-benzene	7.8	--	19	155	180	--	3500	--	15000
1,1,1-Trichloro-ethane	5.6	--	60	260	550	--	10000	--	45000
Nitrates									
Nitrobenzene	15	0.37	0.5	4.9	4.7	100[a]	90	420[a]	400
Nitroethane	15.4	0.97	0.4	2.7	3.8	64	70	290	320
Nitremethane	16.4	--	0.24	2.1	2.3	--	45	--	190

TABLE 6 (CONTINUED)

Permeant	Permachor for Compound	P_f in g/24 hr/0.001 in^2/0.001 in							
		32°F		70°F		130°F		165°F	
		Exp.	Calc'd	Exp.	Calc'd	Exp.	Calc'd	Exp.	Calc'd
Hydrocarbons									
Benzene	5.4-7.6	45	65	440	600	4500	3800	13700	17000
Cyclohexane	7.0-8.0	31.6	29	251	270	3730	3100	15000(a)	14000
Decane	10.0	9.5	6.3	71.2	59	1220	1120	4120	5000
Dipentene	8.9	15	11	128	105	2030	2000	8110	8600
n-Heptane	7.0	48.6	29	270	270	2650	5000	8160	2300
n-Heptene	6.8	--	32	270(a)	300	--	5600	--	25000
n-Hexane	6.0	48	48	350	450	9000	8500	30000	38000
Methylcyclo-hexane	7.0	--	29	275	270	--	5000	--	23000
Octadecane	16.7	--	0.2	1.8(b)	2.0	--	40	--	160
i-Pentane	7.0	48	29	270	270	5000(a)	5000	20000(a)	23000
n-Pentane	5.0	97	80	526	740	15000(a)	4000	60000(a)	62000
Pentene-2	4.8	180	90	695	800	16000(a)	5000	65000(a)	70000
Tetradecane	13.0	1.7	1.4	14.6	13	404	250	1000(a)	1100
Tetradecene	12.8	--	1.5	12(b)	14	--	1200		
Toluene	6.4	58	40	505	370	5775	7000	28700	31000
o-Xylene	7.4	36	24	256	230	3600	4100	16600	19000
p-Xylene	5.8-7.4	85.7	54	486	500	4800	4100	16300	19000

(a) Estimated from log P_f vs 1/T Plots.
(b) Estimated from cup tests.

NOTE: Experimental P_f taken from (30-40 mil) bottle test data from WADC Report,[5] calculated P_f made by Salame using Eq. IX and data from Table 4.

TABLE 7. EXPERIMENTAL AND CALCULATED PERMEABILITY FACTORS FOR LIQUIDS IN HIGH-DENSITY POLYETHYLENES AND POLYPROPYLENE
(adopted from reference 6)

Permeant	Permachor for Compound	Temp., °C	High-Density Polyethylenes				Polypropylene	
			Ziegler-type		Phillips-type			
			Exp'l	Cal'd[a]	Exp'l	Cal'd[a]	Exp'l	Cal'd[b]
Acetic acid	15.5	73	-	0.6	1.0	0.9	-	1.4
		120	-	4.9	6.0	4.9	-	8.9
Acetone	13.8	73	1.5	1.5	1.9	2.1	0.7	3.9
		120	19.0	11.5	8.0	11.5	22.5	25.0
Carbon Tetrachloride	5.8	73	68.0	85.0	98.0	120.0	460.0	456.0
		120	670.0	660.0	637.0	660.0	2800.0	2960.0
Dipentene	8.9	73	13.0	17.8	25.6	25.0	75.0	72.5
		120	139.0	138.0	136.0	138.0	409.0	468.0
Ethyl acetate	12.0	73	3.9	3.7	4.5	5.2	14.8	11.2
		120	51.0	29.0	43.0	29.0	140.0	72.5
Methanol	17.5	73	0.3	0.2	0.2	0.3	0.2	0.4
		120	4.8	1.8	5.2	1.8	3.9	2.7
n-Butyl ether	9.4	73	12.7	13.8	21.0	19.5	-	53.8
		120	110.0	107.0	112.0	107.0	-	347.0
n-Decane	9.3	73	11.4	14.5	-	20.4	57.0	56.2
		120	98.0	112.0	-	112.0	390.0	363.0
Toluene	6.4	73	80.0	63.0	118.0	89.0	360.0	323.0
		120	500.0	490.0	496.0	490.0	1954.0	2090.0

(a) Using Equation IX: $\log P_f = K-[0.22(I)]$ where K is 3.21 and 3.36 for Ziegler and Phillips at 73°F, respectively and 4.10 for both at 120°F.

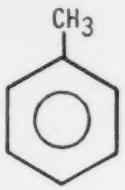
(b) Using Equation IX: $\log P_f = K-[(M)(I)]$ where K is 4.17 at 73°F and 4.98 at 120°F for polypropylene and M = 0.26 (see Figure 5).

TABLE 8. COMPOUNDS YIELDING LESS ACCURATE PERMEABILITY FACTORS BY USE OF PERMACHORS
(adopted from reference 6)

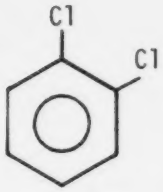
Cause of Deviation	Effect of Deviation on P_f	Examples		
		Organic Liquids	Exp. P_f	Cal'd P_f
1. Perfect symmetry of polar groups cancels out any net polar charge	increases	Hydroquinone	0.36	0.10
		CCl_4	610.0	500.0
2. Lower temperature decreases effective polarity of molecule	increases	Methyl ethyl ketone	3.7 (32^oF)	1.8
		Acetaldehyde	3.4 (32^oF)	0.8
3. Lower temperature causes phenyl group to become more rigid and less able to mobilize.	decreases	Benzaldehyde	0.37 (32^oF)	1.1
		Benzoic acid	0.07 (70^oF)	0.3
4. Chemical changes may take place at higher temperatures due to oxygen and moisture entering the permeant through the polyethylene	increases or decreases	Acetic anhydride (forms some acetic acid which has a higher P_f)	213 (165^oF)	95
5. Intramolecular hydrogen-bonding between segments of the same molecule essentially reduce the size of the permanent molecule	increases	Diacetone alcohol	0.3 (70^oF)	0.01
		Diethylene glycol	0.76 (165^oF)	0.02
		Ethylene glycol	1.26 (165^oF)	0.2
		Ethylene glycol-monobutyl ether	180 (165^oF)	87
		Glycerin	1.6 (165^oF)	0
6. Changing of shape factor with increasing temperature	increases	sec-Butyl alcohol	278 (165^oF)	87
		tert-Butyl alcohol	236 (165^oF)	32

Additional examples:

Computation of Permachors

(a) 

1 mono phenyl group @	i =	5.4
1 carbon @	i =	1.0
	I =	6.4

(b) 

1 ortho phenyl group @	i =	5.4
2 chloro groups @	2 i =	2.4
	I =	7.8

(c) Cl-CH_3-C(=O)-OH

1 Cl @	i =	1.2
1 aliphatic acid group @	i =	13.5
2 carbons	2 i =	2.0
	I =	16.7

(d) CH_3-C(=O)-CH_3

3 carbons @	3 i =	3.0
1 keto group @	i =	10.8
	I =	13.8

(e) CH_3-C(=O)-OH

2 carbons @	2 i =	2.0
1 aliphatic acid @	i =	13.5
	I =	15.5

P_f values for these compounds are given below assuming 73°F and use of Phillips type-HDPE. From Table 5, K = 3.36 @ 73°F and M = 0.22. P_f would be calculated as follows:

$$\log P_f = 3.36 - (0.22\ I) \text{ or } P_f = \log^{-1}[3.36 - (0.22\ I)]$$

Compound	I	P_f (Calculated) (A)	P_f (Experimental)[6] (B)	Absolute (%) Deviation |(B - A)/B| x 100%
toluene	6.4	90	118	24
1,2-dichlorobenzene	7.8	44	--	--
chloroacetic acid	16.7	0.49	--	--
acetone	13.8	2.1	1.9	11
acetic acid	15.5	0.89	1.0	11

Usefulness of Permachor Method

In the absence of relevant experimentally derived data, the Permachor Method provides a means to estimate permeabilities of organic liquids through polyethylene and polypropylene. DOT and NBS have established the validity of the method and have expanded its applicability to various types of polyethylenes. DOT/NBS have developed a concept called the "effective C atom number" as a calibration method. It is reported that once the C atom number of a liquid is derived from measurements with one type of PE, permeability through other PE resins can be predicted.[29] If DOT/NBS concepts and data were to be used in liner technology, modifications would be required because DOT/NBS developed data using resins different from liner

resins and many equations have geometric parameters not applicable to liner use.

Since the Permachor Method was developed for pure liquids, it should be most readily employable for PE liner applications involving exposures to a concentrated organics. A few examples might be (a) if PE is used as a secondary liner for confining leaks of organics from underground storage tanks, or (b) when a buried or immersed liner is exposed to a fairly concentrated solvent. In such cases, given the type of organic, physical description, liner type, and methodology of this section, the permeation rate could be estimated. Such data may be useful for both design and in remedial action measures.

The probability of adapting the Permachor Method for concentrated organic/aqueous mixtures appears promising in light of studies by August and Tatzky. Their work shows that organic species present in aqueous systems will permeate PE essentially to the exclusion of water.[40] It was found that permeabilities of such organics in water closely correlated with their permeabilities as pure solvents. Correlation of Permachor data for organic/aqueous solutions would be required.

The usefulness of the method has been demonstrated for polar and non-polar organic liquids and for some multifunctional compounds (e.g., glycerin). On these bases, the Permachor Method should be applicable to the above types of organic fluids although the method will be less accurate for those compounds that tend to ionize in solution or that manifest those deviations given in Table 8.

According to the August and Tatzky study for HDPE, the measured values for organics present in very low concentrations "are only lower than the permeation rates of pure solvents by a factor of 1/20 to 1/30." (See Table 9 for permeation data.) Thus, the potential for adapting the Permachor Method to estimate the transport of components from such mixtures appears

TABLE 9. PERMEATION RATES OF PURE ORGANIC SOLVENTS AND DILUTE ORGANIC-AQUEOUS MIXTURES
(adopted from reference 41)

Organic Solvent	Weight % Concentration of Organic Solvent in Water	Permeation Rates in $g/m^2 \cdot day$						
		$HDPE_{1.0}$*	$HDPE_{1.5}$	$HDPE_{2.5}$	$HDPE_{2.0}$	$HDPE_{2.7}$	$ECB_{2.6}$	$EPDM_{1.8}$
Acetic acid	100							
	5	<0.001					<0.001	<0.001
Acetic acid ethylester	100	1.9			1.3			
	5						8	60
Acetone	100							
	5	<0.001					0.2	2
Carbon tetrachloride	100	35						
	0.08						2	12
Chloro-benzene	100	29			13			
	0.05							
Chloro-form	100	65						
	0.08						48	
i-Octane	100	1.7		0.4	0.7			
	0.001	<0.001					0.7	
Methanol	100							
	5	<0.001					<0.001	0.1
Tetrachloro-ethylene	100	60	38	20	41	22		
	0.015							
Tetrahydro-furan	100	24						
	5							
Trichloro-ethylene	100	150	86	47	109	81		
	0.1	6					8	
Toluene	100	40	19	10	18	13		
	0.05	2					15	
Xylene	100	32	16	9	12	9		
	0.02	1.6					7	3

TABLE 9. (CONTINUED)

Organic Solvent	Weight % Concentration of Organic Solvent in Water	Permeation Rates in $g/m^2 \cdot day$						
		PVC-$p_{0.8}$	PVC-$p_{1.0}$	PVC-$p_{1.5}$	PVC-$p_{2.0}$	PVC-p/PEC$p_{1.5}$	PEC$_{1.5}$	PEC/PE$_{1.5}$
Acetic acid	100							
	5				<0.1			
Acetic acid ethylester	100							
	5			79	83	8	23	
Acetone	100							
	5				1.0			
Carbon tetrachloride	100							
	0.08				1.4			
Chloro-benzene	100							
	0.05							
Chloro-form	100							
	0.08				53			
i-Octane	100							
	0.001				<0.001			
Methanol	100							
	5				<0.1			
Tetrachloro-ethylene	100							
	0.015							
Tetrahydro-furan	100							
	5							
Trichloro-ethylene	100							
	0.1						6	
Toluene	100							
	0.05	8	17	7	4	5 15	5	8
Xylene	100							
	0.02	5	1.4	4.4	2	2.5	2.5	4

promising but would have to be established; permeation rates for mixtures would be of concern in liner technology guidelines for estimating effluent compositions and volumes. Dilute solution absorption studies could serve as a useful data base to complement Permachor data in estimating organic transport rates (Appendix C).

Because (a) nonelectrolytes are prevalent pollutants in landfill and surface impoundment environments (see Griffin and Shimp,[54] Appendix D) and because (b) organic permeation rates can be significantly higher than the de minimis definition of 1 gal/acre·day, as indicated by the data below taken from Table 9, the definition of de minimis should be altered to address such differences. From this data, it should be noted that even organics present in dilute solutions/dispersions can permeate commercial types of polymeric liners at rates exceeding 1 gal/acre·day.

	Concentration in Aqueous Solution	Permeation Rate $g/m^2 \cdot day$	Permeation Rate gal/acre·day
Trichloroethylene:			
pure solvent (HDPE/1.0 mm thick)	100 %	150.0	107.0
in water (HDPE/1.0 mm thick)	0.1 %	6.0	6.4
Acetone (PVC/2.0 mm thick)	5 %	1.0	1.1
Chloroform (EPDM/2.6 mm thick)	0.08 %	48.0	51.0
Chloroform (PVC/2.0 mm thick)	0.08 %	53.0	57.0

FLOW THROUGH LINER FLAWS

The effects of flaws on liner performance are addressed in this section. Based on fluid flow models, effluent loss by flow through flaws is estimated and compared with permeation and a benchmark value of 4.3 $g/m^2 \cdot day$ (4 gal/acre·day). For aqueous liquids, our analysis indicates that both capillary and larger flaws adversely affect liner performance. The effects of such flaws can, however, be mitigated by using a low permeability subbase with a liner.

Equations describing fluid flow through liner flaws are typically derived from equations describing fluid flow through conduits. Simple models assume that the holes are cylindrical and the layer under the FML is permeable (i.e., entire landfill is free draining). Based on these assumptions, models analyzing cases of noncircular flaws and drainage limited by impermeable soil beneath the flexible membrane liner have been developed for predicting leachate quantities generated from landfills.[55-58] Rather than predicting leachate generated from landfills, the following analysis focuses on evaluating the performance of the liner independent from its use in the landfill. The rationale for using the assumption of a free draining liner is to compare the leakage rate through liner flaws with the permeability of a flawless liner and to, thus, assess liner performance. The equations do not yield accurate estimates for landfill leachate generation and should not be used for such purposes. To estimate leachate generation rates, the equations would be combined with the permeability of the soils that would be used in conjunction with the liner in a series type calculation.

As discussed previously, a major difference in contaminant loss by flow through liner flaws and from permeation is the absence of permselectivity in the former. To estimate contaminant loss by flow through flaws, it can be assumed that the effluent composition is identical to the

composition of the bulk liquid contained in the landfill. Thus, contaminant loss by effluent flow through liner flaws is simply the product of the bulk contaminant concentration and the effluent flow rate.

For analyzing circular flaws in free draining liner systems, fluid flow through conduits is based on the Bernoulli equation for large flaws and the Hagen-Poiseuille equation for smaller flaws. The difference between the two equations is based on the influence of drag from the walls of the liner flaw. The technical literature is not specific regarding the hole sizes to which each equation applies. The concept of a "boundary layer" is used here to estimate the range of hole diameters to which each equation applies. The physical phenomena affecting the fluid flow rate can be determined by the analysis of these equations.

Flow Through Small Flaws

Capillary flow has been modeled in the literature by the Poiseuille equation:[59]

$$Q = (UGzd^4)/(128nl) \qquad (X)$$

where Q = volumetric flow rate, cm^3/sec
U = fluid density, gm/cm^3
G = gravitational acceleration, 981 cm/sec^2
z = hydraulic head, cm
d = hole (capillary) diameter, cm
n = viscosity, gm/cm-sec
l = liner thickness which is equivalent to capillary length, cm

According to the Poiseuille equation, the physical parameters affecting effluent flow through pinholes are: 1) effluent density, 2) hole diameter, 3) hydraulic head, 4) liner thickness, and 5) effluent viscosity. Results

from the flow rate calculations for dilute aqueous solutions over a range of hole diameters, hydraulic heads, and liner thicknesses are shown in Tables 10-15. Tables 10-12 present the results where the hydraulic head, z, is 3.05 m (10 feet) and the effluent density and viscosity are equivalent to that of water at 20°C. Hole diameters range from 0.006 cm to 0.025 cm (2 to 10 mil) and liner thicknesses range from 0.051 cm to 0.152 cm (20 mil to 60 mil). Tables 13-15 present the results of similar calculations with a hydraulic head of 9.14 m (30 feet). The flow rates for individual holes modeled by the Poiseuille equation range from 2.0×10^{-3} cm^3/sec (in the case of a 0.006-cm-diameter hole in a 0.15-cm-thick liner) to 5.4 cm^3/sec (for a 0.025-cm-diameter hole in a 0.051-cm-thick-liner). The effluent flows range over three orders of magnitude under the conditions modeled.

Figures 2 and 3 show the effects of liner thickness and hole diameter on effluent flow calculated from the Poiseuille equation. Figure 4 shows the effect of hole diameter on effluent flow calculated from the Bernoulli equation.

Flow Through Large Flaws

The Bernoulli equation for modeling free draining leakage through larger flaws is:

$$Q = C_f a(2Gz)^{1/2} \qquad \text{(XI)}$$

where Q = volumetric flow rate, cm^3/sec
C_f = correction factor, 0.6
a = cross sectional area of flaw, ($3.14\ d^2/4\ cm^2$)
G = gravitational acceleration, cm/sec^2
z = hydraulic head, cm

TABLE 10. POISEUILLE EQUATION

(Based on 305-cm hydraulic head and a 0.051-cm membrane thickness)

Hole Diameter, cm	Hole Area cm^2	Volumetric Flow Rate cm^3/sec
0.006	2.83×10^{-5}	6.0×10^{-3}
0.012	1.13×10^{-4}	9.5×10^{-2}
0.025	4.91×10^{-4}	1.8

TABLE 11. POISEUILLE EQUATION

(Based on 305-cm hydraulic head and a 0.076-cm membrane thickness)

Hole Diameter, cm	Hole Area cm^2	Volumetric Flow Rate cm^3/sec
0.006	2.83×10^{-5}	4.0×10^{-3}
0.012	1.13×10^{-4}	6.4×10^{-2}
0.025	4.91×10^{-4}	1.2

TABLE 12. POISEUILLE EQUATION

(Based on 305-cm hydraulic head and a 0.152-cm membrane thickness)

Hole Diameter, cm	Hole Area cm^2	Volumetric Flow Rate cm^3/sec
0.006	2.83×10^{-5}	2.0×10^{-3}
0.012	1.13×10^{-4}	3.2×10^{-2}
0.025	4.91×10^{-4}	5.9×10^{-1}

TABLE 13. POISEUILLE EQUATION

(Based on 914-cm hydraulic head and a 0.051-cm membrane thickness)

Hole Diameter, cm	Hole Area cm^2	Volumetric Flow Rate cm^3/sec
0.006	2.83×10^{-5}	1.8×10^{-2}
0.012	1.13×10^{-4}	2.9×10^{-1}
0.025	4.91×10^{-4}	5.4

TABLE 14. POISEUILLE EQUATION

(Based on 914-cm hydraulic head and a 0.076-cm membrane thickness)

Hole Diameter, cm	Hole Area cm^2	Volumetric Flow Rate cm^3/sec
0.006	2.83×10^{-5}	1.2×10^{-2}
0.012	1.13×10^{-4}	1.9×10^{-1}
0.025	4.91×10^{-4}	3.6

TABLE 15. POISEUILLE EQUATION

(Based on 914-cm hydraulic head and a 0.152-cm membrane thickness)

Hole Diameter, cm	Hole Area cm^2	Volumetric Flow Rate cm^3/sec
0.006	2.83×10^{-5}	6.0×10^{-3}
0.012	1.13×10^{-4}	9.5×10^{-2}
0.025	4.91×10^{-4}	1.8

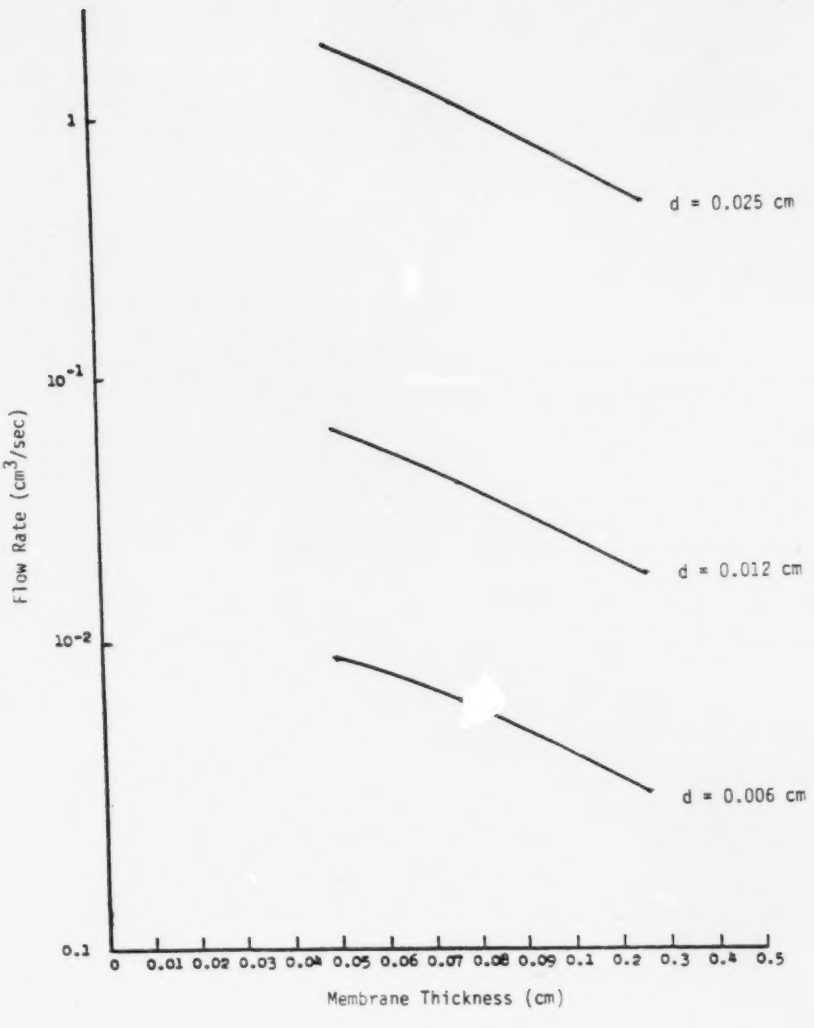


Figure 2. Effluent flow versus membrane thickness using the Poiseuille equation (hydraulic head = 305 cm).

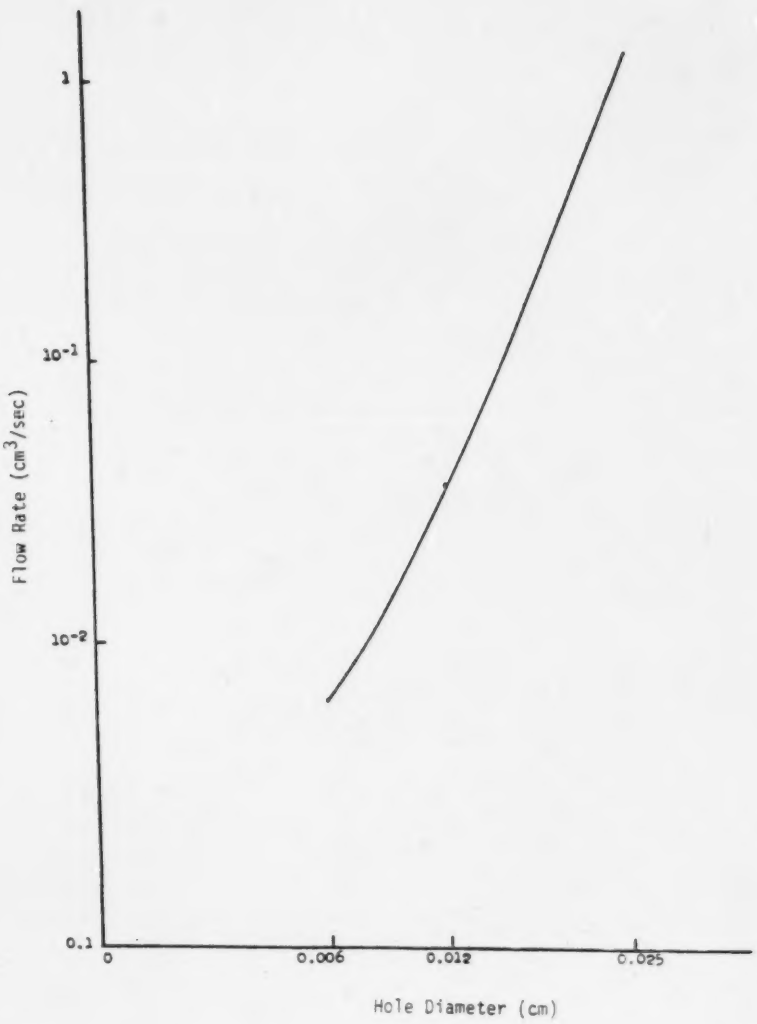


Figure 3. Effluent flow versus hole diameters using the Poiseuille equation (membrane thickness = 0.0762 cm; hydraulic head = 305 cm).

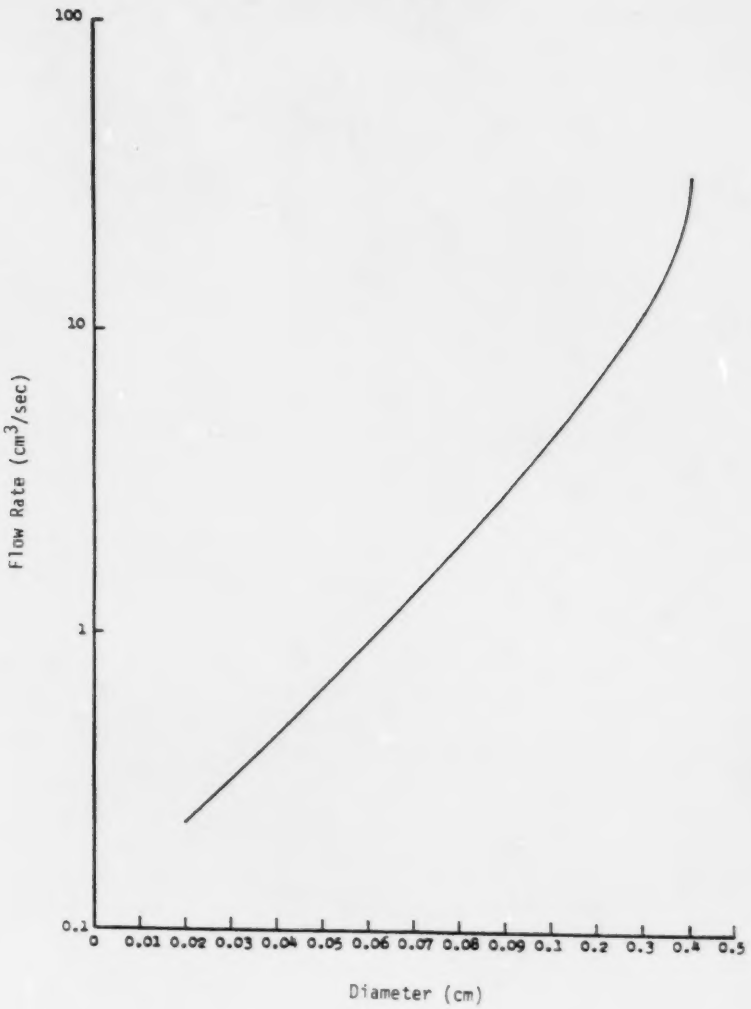


Figure 4. Effluent flow versus hole diameter for larger holes using the Bernoulli equation (hydraulic head = 305 cm).

This equation indicates effluent flow is dependent only on hole diameter and hydraulic head to the one-half power. Tables 16 and 17 show the results of calculations for effluent flow over a range of hole sizes.

TABLE 16. BERNOULLI EQUATION
(Based on 305-cm hydraulic head)

Hole Diameter,cm	Flow Rate, cm^3/sec
0.025	0.24
0.051	0.94
0.076	2.12
0.152	8.47
0.203	15.05
0.305	33.87

TABLE 17. BERNOULLI EQUATION
(Based on 914-cm hydraulic head)

Hole Diameter,cm	Flow Rate, cm^3/sec
0.025	0.41
0.051	1.63
0.076	3.66
0.152	14.66
0.203	26.06
0.305	58.63

Relationship Between the Poiseuille and Bernoulli Equations

Models for leakage through liner flaws are based on either the Poiseuille or the Bernoulli equation. Models for leakage through liner flaws are typically based on circular flaws with the Poiseuille equation describing laminar flow through small holes and the Bernoulli equation describing turbulent flow through large holes. The models do not specify the range of diameters to which the equations apply; however, it has been proposed that "large holes" are holes having a dimension (e.g., diameter if circular) "significantly larger than the geomembrane thickness."[59]

Analysis by Reynold's number indicates that a hole diameter of 0.016 cm (5 mil) is a conservative estimate of the transition size for liner calculations using Poiseuille and Bernoulli equations. The calculation is presented below. In the Poiseuille equation, discharge is directly proportional to the fluid density, hydraulic head, and hole area squared and is inversely proportional to the effluent viscosity and liner thickness. In the Bernoulli equation, discharge is proportional to the hole diameter squared and the square root of the hydraulic head and is independent of the liner thickness, effluent viscosity, and effluent density. Discharge estimated by the Poiseuille equation is considerably higher than flows estimated by the Bernoulli equation at small liner thicknesses and large diameter holes. Although the Poiseuille equation is more conservative for cases involving thin liners, it provides unrealistically large estimates of fluid flow compared with published measurements (discussed below). The point of equivalence, where the discharge calculated by the equations are equal, varies with the liner thickness.

For small holes, the Poiseuille equation would apply assuming laminar flow:

$$Q = (UGzd^4)/(128nl) \qquad \text{(XII)}$$

From the Reynold's Number,

$$N_{Re} = (d\bar{v}U)/n \qquad \text{(XIII)}$$

where d = diameter of pipe, cm
$\bar{v}$ = velocity of fluid, cm/sec
U = density of fluid, g/cm^3
n = viscosity of fluid, g/cm-sec

the transition from laminar to turbulent flow could be expected at N_{Re} = 580.[3]

$$Q = \bar{v}A = (3.14\bar{v}d^2)/4 \qquad \text{(XIV)}$$

From equations (XII), (XIII), and (XIV):

$$Gzd^4/128nl = N_{Re}n/Ud = 3.14d^2/4$$

solving for d:

$$d^3 = [(32)(3.14)N_{Re}n^2l]/(U^2Gz)$$

or

$$d = ([(32)(3.14)N_{Re}n^2l]/U^2Gz)^{1/3}$$

For water at 21^{o}C (70^{o}F):

n = 0.01 g/cm·sec
U = 0.99 g/cm^3

Assuming laminar flow, i.e., $N_{Re} < 580$ through an 0.2032 cm (80 mil) liner thickness in a 914.4 cm (30 ft) head surface impoundment:

$$d_{max} = [(32)(0.01)^2(3.14)(0.203)(580)/(1.00)^2(981)(914.4)]^{1/3} cm$$

$$d_{max} = 0.0115 \text{ cm}$$

$$d_{max} = 0.005 \text{ in}$$

$$d_{max} = 5 \text{ mils}$$

Comparison of these equations for flow through small and large holes using specific values of hole size and hydraulic head has been carried out and analysis of these equations led to the following conclusions:[59]

1) Model shows that leakage due to geomembrane permeability is negligible compared with leakage through holes. Leakage due to "pinholes" is also negligible, unless large number of "pinholes."

2) Flow through liners can be minimized by reducing the hydraulic head through the use of multiple liners.

Comparison of Calculated to Measured Flow Rates

The leak rates calculated by the Bernoulli and Poiseuille equations were compared with measured leak rates reported from two sources, Stone, J.L.,[60] and Brown, K.W., and Thomas, J.C.[39] Tables 18 and 19 present the hydraulic parameters, the measured leak rate, and the calculated leak rates by both Bernoulli and Poiseuille equations for the Proton Decay Experiment[60] and the Texas A&M study.[39]

The tables show that the Poiseuille equation yields unreasonably high estimates compared with the measured values indicating that the flow conditions more closely correlate to those described by the Bernoulli equation. The Bernoulli equation also overestimates the flow when its results are compared with the measured values. The overestimation of the

TABLE 18. LEAK RATES REPORTED IN PROTON DECAY EXPERIMENT

(adopted from reference 60)

	Hydraulic Parameters	Measured Leak Rate, liter/min	Bernoulli, liter/min	Poiseuille, liter/min
Case No. 1	head = 1350 cm hole size = 4.70 cm^2 liner thickness = 100 mil	28	275	1.4×10^8
Case No. 2	head = 1900 cm hole size = 1.75 cm^2 liner thickness = 100 mil	>40	122	2.2×10^7
Case No. 3	head = 1700 cm hole size = 3.4 cm^2 liner thickness = 100 mil	8	224	6.5×10^6

TABLE 19. LEAK RATES REPORTED IN TEXAS A&M STUDY

(adopted from reference 39)

Hydraulic Parameters	Measured Leak Rate, cm^3/sec	Bernoulli, cm^3/sec	Poiseuille, cm^3/sec
head = 100 cm hole size = 1.2 cm^2 liner thickness = 36 mil	250	319	1.9×10^6

calculated to the measured value is attributable to the assumption of a free draining system. In Case No. 2 of the Proton Decay Experiment (Table 18), where there is less than one order of magnitude between the values based on the Bernoulli equation and measured values, the system was characterized by a void under the hole and thus more closely matched the free draining condition than the other cases.

For a 1-acre liner 0.091-cm (36 mil) thick[8] a flawed area of 5 x 10^{-6}% of the total liner would generate leakage equivalent to that of water permeation through PE in a free draining system. For some organic liquids, such as TCE, the permeation rate is significantly higher than that of water and the flow rate through flaws is nearly equivalent to that of water. In those cases, a greater number of holes would be required to produce effluent loss equivalent to that from permeation.

When leakage values are compared with permeation values for organic liquids, remember that the permeation rates of organics vary according to the type of permeant. The permeation rate for TCE through HDPE liners is approximately four orders of magnitude greater than that of water.[8] Based on Brown and Thomas, the leakage of TCE would be roughly equivalent to that of water. Thus, permeation of organics could generate more leachate than is generated by flow through a limited number of small holes. For example, estimates of TCE permeation through PE (100% TCE) are 110 gal/acre·day, approximately equivalent to one 0.16-cm-diameter hole over a permeable subbase (305 cm head). Values for permeation of organics through liners backed by a subbase are not reported in the literature. Based on the liner subbase effect on leakage of water, however, it appears that such a system can reduce organic loss by flow to an acceptable level.

The work of Brown and Thomas supports the conclusions of Giroud in respect to leakage and permeability of aqueous liquids, i.e., that leakage by permeation is miniscule compared with leakage by flow through flaws.[59] However, the conclusion may not be true for organic liquids.

A Comparison of Calculated Flow Rates to a De Minimis Benchmark of Four Gal/Acre·Day

According to Brown and Thomas, the leakage estimation techniques are subject to uncertainty in measuring the gap between the liner and the subbase in the field and this parameter can change over time if the subbase below the hole erodes.[39] Thus, it will be difficult to correlate a leakage rate to a specific size and number of holes from site to site.

The Texas Agricultural and Engineering Experiment Station has completed a study entitled "Quantification of Leak Rates Through Holes in Landfill Liners."[40] In the study, the investigators constructed a permeater for measuring the flow of water through flaws in liners.

Their permeater allows systematic study of the effects of polymeric liner type and thickness, flaw size and shape, hydraulic head, and subbase conductivity. The flow of liquids was found to be dependent on the size and shape of the flaw, the liquid head, and hydraulic conductivity of the subbase.

Values for maximum leakage were approximately 200 cm^3/sec for a 0.08-cm-thick HDPE liner installed over a permeable gravel subbase with holes and with areas ranging from 0.16 to 1.27 cm^2 at hydraulic heads of 50 and 100 cm. These leakage rates exceed the benchmark of 4 gal/acre·day. For example, according to the measured data, one 0.16 cm hole in a 16 acre liner would approach regulatory guidelines of "de minimis." But even under a good construction quality assurance program, polymeric liners may have up to 1 or 2 small holes per acre of liner.[61] Essentially, only flawless liners would be acceptable for applications with permeable subbases.

For liners over low conductivity subbases, the flow from the entire system is significantly less than for cases where the liner is covering

highly permeable soil. Values for 1.27 cm^2 holes over 10^{-4} cm/sec and 10^{-6} cm/sec subbases are 2.8 cm^3/sec and 2.9×10^{-3} cm^3/sec, respectively. The leakage rate through a hole in FMLs with 10^{-6} cm/sec subbases are below the de minimus values of the proposed regulatory guidelines. For systems utilizing 10^{-4} cm/sec subbases, one 1.27-cm-diameter hole in 12 acres is equivalent to the proposed standard. However, for systems utilizing 10^{-6} cm/sec subbases, approximately sixty 0.2 cm diameter holes would be allowable in an acre (head = 100 cm).

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APPENDIX A
LITERATURE SEARCHING TECHNIQUES

A wide range of published information was reviewed and technical specifications in vendor publications pertaining to liners were noted. The information in the field of technology concerning polymeric membranes, particularly that portion pertaining to material transport, served to underpin polymeric liner characterizations.

Pertinent information has mainly been published since 1964. A search strategy was developed for compilation of papers, reports, brochures, and other relevant information The techniques utilized are as follows:

- hand searching the following library references:

Chemical Abstracts	(1980 - 1984)
Applied Science & Technology	(1982 - 1984)
Dissertation Abstracts International	(1973 - 1980)

- developing a key word strategy from the hand search for assembling data relating to the study and inputting them into a computer to retrieve relevant abstracts. The following key words were used:

Plastic Liner	Waste
Plastic Film	Polymer
Plastic Film Bond	Polyethylene (HDPE, LDPE, LLDPE), PVC, EPDM, ELPO, ECO, CPE, PEEL
Plastic Film Weld	Leaching
Film	Landfill
Liner	Permeation
Membrane	Flow

Leak	Transport
Flaw	Hole

- Reviewing full texts of key papers.

The following list includes each data file and years searched in this study.

NTIS	(1964+)
Compendex	(1970 - 1984)
Environmental Bibliography	(1974+)
Chem. Industry Notes	(1974+)
SCISEARCH	(1985)
ENVIRONLINE	(1970 - 1984)
Pollution Abstracts	(1970 - 1984)
World Textiles	(1970+)
SCISEARCH	(1974 - 1983)
FLUIDEX	(1973+)
AQUALINE	(1964+)
Textile Technology Index	(1978 - 1984)
Occupational Safety & Health	(1973 - 1984)
Federal Research in Progress	(1984)
CA Search	(1967+)

APPENDIX B
PERMEATION DATA FOR POLYMERIC FILMS, MEMBRANES, AND LINERS

TABLE B-1. WATER VAPOUR TRANSMISSION[a]
(adopted from references 44 and 62)

Plasticizer	g/(100 in^2/24 hr)
Dioctyl phthalate	1.15
Octyl decyl phthalate	1.35
Trioctyl phosphate	1.61
Cresyl diphenyl phosphate	1.91

(a) Geon 103.EP--0.004-inch PVC film.

TABLE B-2. GAS PERMEABILITY[a] THROUGH PVC-FILM
(adopted from references 44 and 62)

Polymer Compound	Dioctyl Phthalate Plasticizer (100 parts polymer)	Gas	Permeabilities at: 20°C	30°C	40°C
Geon 101.EP	-	CO_2	0.96	0.102	0.109
		H_2	0.32	0.36	0.40
Geon 101.EP	5 phr	CO_2	4.0	3.85	3.7
		H_2	12.2	11.3	10.8
Geon 101.EP	20 phr	CO_2	140.0	130.0	118.0
		H_2	8.5	8.6	8.8
Geon 202	31 phr	CO_2	0.155	0.310	0.610
		H_2	0.92	0.20	0.40

(a) Permeability in $cm^3/(cm^2 \cdot sec/cm\ Hg \times 10^{-9})$

TABLE B-3. PERMEABILITY CONSTANTS[a] FOR POLYMERS TO VARIOUS GASES
(adopted from reference 63)

Polymer	Nitrogen	Oxygen	Carbon dioxide	Water
Polyethylene (density 0.922 g/cm^3)	20	59	280	800
Polyethylene (density 0.954 g/cm^3)	3.3	11	43	180
Poly(vinylidene chloride) (Saran)	0.01	0.05	0.29	14-100
Ethylcellulose	84	265	410	130,000
Cellulose acetate	2.28	7.8	23.8	75,000

(a) [cm^3 at 0^{o}C, 1 atm] [cm]/([cm^3] [sec] [cm Hg x 10^{11}]).

TABLE B-4. PERMEABILITY DATA OF FIVE GLOVE MATERIALS
(adopted from reference 64)

Sample/Thickness	Temp., °C	Relative Humidity, %	Permeation Coefficient $\frac{\text{std cm}^3 \cdot \text{cm}}{\text{cm}^2 \cdot \text{sec} \cdot \text{Torr}}$	Diffusivity $\frac{\text{cm}^2}{\text{sec}}$	Solubility $\frac{\text{std cm}^3}{\text{cm}^3 \cdot \text{Torr}}$
Butyl rubber glove, 0.020 in.	39	78%	8.6×10^{-10}	3.3×10^{-9}	0.44
Sample from Norton Co., 0.020 in.	39.5	84%	6.6×10^{-10}	3.1×10^{-9}	0.29
Neoprene Sample from Norton Co., 0.018 in.	39	83%	161×10^{-10}	3.2×10^{-9}	4.54
Hypalon Sample from Norton Co., 0.017 in.	38	80%	113×10^{-10}	9.0×10^{-9}	1.25
EPDM/Butyl Rubber Laminated glove, 0.035 in.	37.2	69%	7.3×10^{-10}	5.1×10^{-9}	0.11
Hypalon/Neoprene Laminated sample from Norton Co., 0.035 in.	38	65%	114×10^{-10}	6.2×10^{-9}	2.9

TABLE B-5. ORGANIC LIQUID PERMEATION OF BARRIER POLYMERS
(adopted from reference 65)

Polymer	Polymer Class	Liquid permeation rates[a] kg·cm/(km²·day)		
		Ethanol	Heptane	Ethyl acetate
Lopac	nitrile	<20	<20	<20
Barex	nitrile	25	<20	20
Cycopac	nitrile	<20	<20	20
Kel-F	halogenated	<20	20	<20
Poly(ethylene terephthalate)	polyester	28	<20	61
Poly(viny chloride)	halogenated	<20	<20	78,000 (+ attack)
Acetal	--	60	20	470
XT Polymer	acrylic	2,000 (+ attack)	<20	attack

(a) Permeation rates were measured for 25°C; other experimental data is not given in reference.

TABLE B-6. PERMEABILITY PROPERTIES OF HIGH-BARRIER POLYMERS
(adopted from reference 65)

Polymer	Polymer Class	Permeation rates		
		Oxygen[a]	Carbon dioxide[a]	Water[b]
Poly(vinylidene chloride)	halogenated	0.4	1.2	7.9
Lopac[c]	nitrile	3.9	12	200
Barex	nitrile	4.3	12	240
Cycopac	nitrile	4.3	16	200
Saran wrap	halogenated	5.1	18	20
Epoxy (bisphenol A; amine cure)	thermoset	12	35	160
Kel-F (polychlorotrifluoroethylene)	halogenated	13	47	12
Trogamid T	polyamide	18	59	205
Kynar [poly(vinylidene fluoride)]	halogenated	18	59	39
Poly(ethylene terephthalate)	polyester	20-39[d]	47-79[d]	80-160[d]
Nylon-6,9; nylon-6,10	polyamide	22	47	240
Phenoxy [poly(phenylene oxide)]	aromatics	28	59	180
Poly(vinyl chloride)	halogenated	31-59[e]	79-157[e]	80-120[e]

(a) At 23°C (100% relative humidity), $(m^3 \cdot m)/(m^2 \cdot day \cdot PPa)$. To convert PPa to bar, multiply by 10^{10}.
(b) $kg \cdot cm/(km^2 \cdot day)$ at 38°C (100% relative humidity).
(c) Acrylonitrile (70%)-styrene copolymer used for manufacturing Monsanto Cycle-Safe container.
(d) Depends on exact level of crystallinity and orientation.
(e) Depends on exact compound formulation.

TABLE B-7. PERMEATION RATES OF POLYMERS SHOWING EITHER GOOD GAS OR GOOD LIQUID BARRIER PROPERTIES BUT NOT BOTH
(adopted from reference 65)

Polymer	Polymer class	Permeation rates		
		Oxygen[a]	Carbon dioxide[a]	Water[b]
Good gas barrier:				
Poly(vinyl alcohol) (dry)	hydroxylic	0.04[c]	0.12[c]	79,000
Cellophane (dry-uncoated)	cellulosic	0.5 [c]	1.2 [c]	14,000
Good water barrier:				
High-density polyethylene	olefin	433	1,180	20
Polypropylene	olefin	590	1,770	20
Teflon (polytetrafluoroethylene)	halogenated	866	2,360	10
Polybutene	olefin	1,300	3,940	60
Low-density polyethylene	olefin	1,890	5,900	60
Surlyn ionomer	modified olefin	2,165	7,870	100
Butyl rubber	halogenated	5,900	>15,000	80

(a) At 23°C (0% relative humidity), $(m^3 \cdot m)/(m^2 \cdot day \cdot PPa)$. To convert PPa to bar, multiply by 10^{10}.
(b) $kg \cdot cm/(km^2 \cdot day)$ at 38°C (100% relative humidity).
(c) These values are considerably higher (and considered nonbarrier) when measured at 50%relative humidity conditions.

TABLE B-8. PERMEATION THROUGH 4-OUNCE POLYETHYLENE BOTTLES[a]
(adopted from reference 29)

Bottle	Temperature °C	Chemical	Molecular Weight	Average 2-week Weight Loss, gm	Permeation Range, mol/m²·24 hr @ 1 mm thickness	
	40	Trichlorobenzene	181.45	86.2	2.17	2.20
		o-Dichlorobenzene	147.00	96.7	2.94	3.12
	50	Empty		00.0		
		Hydrofluoric acid[b]	20.01	0.2	.03	.03
		Butyl stearate	340.59	1.3	.01	.03
Type #1 (LDPE)		Hydrochloric acid[b]	36.46	1.4	0.17	0.17
		Diphenyl methane	168.24	14.0	0.35	0.41
		Butyl benzoate	178.23	15.6	0.36	0.44
		Tetradecane	198.40	25.3	0.54	0.64
		Trichlorobenzene	181.45	169.7	3.93	4.68
		o-Dichlorobenzene	147.00	158.0	4.66	5.23
Type #2 (HDPE)	50	Trichlorobenzene	181.45	20.6	0.44	0.47
		o-Dichlorobenzene	147.00	22.9	0.62	0.62
	60	Butyl stearate	340.59	0.3	.01	.01
		Diphenyl methane	168.24	24.1	0.54	0.79
Type #1 (LDPE)		Butyl benzoate	178.23	29.8	0.64	0.89
		Tetradecane	198.40	44.2	0.91	1.14

(a) Permeation rates were determined by ASTM D 2684-73 (modified); bottles were filled with ladings to about 3/4 full (100 to 200 grams 100 grams of lading) and bottle weights were monitored at the test temperatures in a constant temperature chamber.

(b) Bottles were blow molded with the following thicknesses:
Type # 1 - 0.86 to 0.89 mm side wall
Type # 2 - 0.69 to 0.71 mm side wall
The caps on these bottles were sealed with epoxy rather than a silicone rubber adhesive.

TABLE B-9. TEMPERATURE EFFECT ON PERMEABILITY OF POLYMER SHEETS TO WATER AND WATER VAPOR
(adopted from reference 4)

Polymer Film	Film Thickness, mm		Permeability[(a)] 25°C	45°C	65°C	85°C	95°C
Poly(chloro-trifluoro ethylene		w	1.5	187	780		
	157	w	1.5	172	780		
Polypropylene	79	w	8.7	147	587	2528	3555
		wv	6.8	101	565	2489	3500
Tetrafluoro-ethylene	45	w	1.3	180	322	2457	4254
		wv	0.7	21	197	2357	4200
Polyethylene-terephthalate (Saran)	47	w	2.3	220	887	5078	6204
		wv	0.9	206	857	4976	5041
Poly(vinyl-fluoride)	102	w	11	260	2213	9118	13756
		wv	9	206	1469	8404	13345
Poly(vinyl-chloride)	50	w	9	81.5	598	4890	-
Polyethylene	300	w	3	150	618	2460	2645
		wv	3	147	618	2459	2640

(a) Permeability units and measurement conditions are not specified in reference.

NOTE: w = water; wv = water vapor

TABLE B-10. WATER VAPOR TRANSMISSION (WVT) RATES OF POLYMERIC MEMBRANE LINERS
(adopted from reference 8)

Polymer	Thickness, mm	WVT[a], g/m^2·day
Butyl rubber	0.85[b]	0.384
	0.85[c]	0.020
	1.85	0.097
Chlorinated polyethylene	0.53	0.643
	0.79[d]	1.400
	0.79[e]	0.320
	0.85	0.264
	0.94	0.305
	0.97	0.643
Chlorosulfonated polyethylene	0.74	0.333
	0.76	0.663
	0.89	0.438
	0.91	0.748
	0.94	0.422
	1.07	0.252
Elasticized polyolefin	0.72	0.142
Epichlorohydrin rubber	1.160	20.18
	1.650	14.30
Ethylene propylene rubber	0.51	0.270
	0.94	0.190
	1.70	0.172
Neoprene	0.51	0.304
	0.91	0.473
	1.27	0.429
	1.59	0.237
Nitrile rubber	0.76	5.51
Polybutylene	0.69	0.084
Polyester elastomer	0.20	10.50
Linear low density polyethylene	0.76	0.0573
High density polyethylene	0.80	0.0172
	2.44	0.0062
	0.86	0.0472
Poly(vinyl-chloride)	0.76	1.94
	0.79	1.85
	0.28	4.42
	0.51	2.97
Saran film,0.5 mil	0.013	0.563

(a) WVT rates were determined by ASTM E96, Procedure BW; water vapor pressure gradient across membrane of 100% RH (inside cup) to 50% RH (outside cup, 23°C).
(b) Matrecon serial number 163R.
(c) Matrecon serial number 57.
(d) Matrecon serial number 135.
(e) Matrecon serial number 77.

TABLE B-11. SOLVENT VAPOR TRANSMISSION (SVT) RATES OF POLYMERIC MEMBRANE LINERS
(adopted from reference 8)

Polymer	Thickness mm	SVT, $g/m^2 \cdot day$(a)				
		Methyl alcohol	Acetone	Cyclohexane	Xylene	Chloroform
Chlorosulfonated polyethylene	1.07-1.12	...	221	...	...	...
Elasticized polyolefin	0.53-0.61	2.10	8.62	760	359	3230
High density polyethylene	0.77-0.83	0.16	0.56	11.7	21.6	54.8
	2.42-2.81	...	...	...	6.86	15.8
High density polyethylene-alloy	0.53	...	...	...	295	...
	0.86-0.88	0.50	2.19	151	212	506
	0.97	...	...	...	220	...
Low density polyethylene	0.74-0.76	0.74	2.83	161	116	570
Polybutadiene	0.64-0.74	0.35	1.23	616	178	2120
Teflon	0.10	0.34	1.27	0.026	0.16	20.6

(a) SVT rates were determined by ASTM E96 (modified); SVT occured as a result of concentration gradient across the membrane by the presence of saturated solvent atmosphere within the cup and the essentially zero level outside the cup.

TABLE B-12. POUCH TEST OF MEMBRANES WITH 5% NaCl AS THE TEST LIQUID
(adopted from reference 8)

Polymer[a]	Exposure Time, days	Weight Change, g			Water Transmission, $g/m^2 \cdot day$
		Empty Pouch	Filled Pouch	Pouch Contents	
Chlorinated polyethylene 86	316	3.60	4.02	0.42	0.291
Chlorosulfonated polyethylene 6R	1151	6.97	10.23	3.26	0.069
Chlorosulfonated polyethylene 55	315	5.35	4.70	-0.65	-0.002
Elasticized polyolefin 36	1151	-0.01	2.32	2.31	0.049
Low density polyethylene 21	315	-0.04	0.86	0.81	0.078
Polybutadiene 98	316	0.14	0.65	0.51	0.043
Poly(vinyl-chloride) 17	1115	0.19	11.00	10.81	0.238
Poly(vinyl-chloride) 19	315	-0.60	1.77	2.37	0.214
Poly(vinyl-chloride) 59	1115	0.19	11.00	10.81	0.238

(a) Number = Matrecon serial number; R = fabric reinforced.

TABLE B-13. WATER VAPOR PERMEABILITY THROUGH BUTYL RUBBER FILM
(adopted from reference 64)

Relative Humidity	Temp., °C	Permeability std. $\frac{cm^3 \cdot cm}{cm^2 \cdot sec \cdot Torr}$
90 ± 5%	30	$12.x10^{-10}$
0 - 90%	37.5	$11.x10^{-10}$
66%	36	$7.1x10^{-10}$
50%	37	$4.6x10^{-10}$
80%	39	$7.6x10^{-10}$

TABLE B-14. WATER VAPOR AND GAS TRANSMISSION RATES AS A FUNCTION OF FILM THICKNESS
(adopted from reference 4)

	Water Vapor[a]			CO_2[a]		
Polymer Film	1 mil	2 mils	3 mils	1 mil	2 mils	3 mils
Polyethylene (0.922 g/cm³)	420	210	140	55	28	18
Polypropylene	160	80	53	12	6	4
($VC-VCl_2$) copolymer Saran	5.5	2.7	1.8	0.12	0.06	0.04
PVC, rigid	630	320	210	0.4	0.2	0.13

(a) Water vapor and gas transmission rate units and measurement conditions are not specified in reference.

TABLE B-15. POUCH TEST OF MEMBRANES WITH A HIGHLY ACIDIC WASTE AS TEST LIQUID
(adopted from reference 8)

Polymer[a]	Weight Change, g			Water Transmission, g/m2.day
	Empty Pouch	Filled Pouch	Pouch Contents	
Chlorinated polyethylene 86	14.28	100.00	198.70	1.213
Chlorosulfonated polyethylene 85	28.26	58.87	46.57	0.510
Elasticized polyolefin 36	1.03	3.58	1.40	0.017
Poly(vinyl-chloride) 88	11.46	45.43	35.84	0.363

(a) N = Matrecon serial number.
NOTE : Exposure time for all pouch test was 1887 days.

TABLE B-16. FILM PERMEABILITY
(adopted from reference 32)

Polymer	Permeability[a]
Poly(vinyl-chloride)	0.35 - 2.0
Polyvinylidene chloride (Saran)	0.01 - 0.03
Polyethylene (density = 0.91 - 0.92 g/cm^3)	0.04 - 0.08
Polytetrafluoroethylene	0.00
Polychlorotrifluoroethylene	0.00

(a) 10^{-6} mg/24 hr/m^2/mm (@ 21^{o}C, 0% relative humidity)

TABLE B-15. POUCH TEST OF MEMBRANES WITH A HIGHLY ACIDIC WASTE AS TEST LIQUID
(adopted from reference 8)

Polymer[a]	Weight Change, g			Water Transmission, g/m2.day
	Empty Pouch	Filled Pouch	Pouch Contents	
Chlorinated polyethylene 86	14.28	100.00	198.70	1.213
Chlorosulfonated polyethylene 85	28.26	58.87	46.57	0.510
Elasticized polyolefin 36	1.03	3.58	1.40	0.017
Poly(vinyl-chloride) 88	11.46	45.43	35.84	0.363

(a) N = Matrecon serial number.
NOTE : Exposure time for all pouch test was 1887 days.

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Polytetrafluoroethylene	0.00
Polychlorotrifluoroethylene	0.00

(a) 10^{-6} mg/24 hr/m^2/mm (@ 21^{o}C, 0% relative humidity)

APPENDIX C
ABSORPTION FROM DILUTE SOLUTIONS

A property of concern in film packaging and barrier applications is that of absorbing organic molecules from dilute solutions. In many cases, these can be large bulky organic molecules dispersed/dissolved in water. This phenomenon is called dilute solution absorption and it is, in most cases, directly related to the barrier properties of the polymer. Dilute solution absorption is carried out by monitoring the depletion of the organic compound under study from a solution of the compound in contact with the polymer. A solution (usually below 1%) of the compound in water or water-alcohol mixture is sealed in a bottle or container made of the polymer, and the concentration of the compound is measured by sampling the contents as a function of time. Some organic compounds used as models for dilute solution absorption studies are shown in Table C-1. Some dilute absorption results, comparing polyethylene and poly(vinyl chloride), are shown in Table C-2.

TABLE C-1. SOME ORGANIC COMPOUNDS USED AS MODELS FOR DILUTE-SOLUTION ABSORPTION STUDIES
(adopted from reference 65)

Alchohol

ethanol
eugenol
linalool
menthol
methyl salicylate
p-chlorothymol
phenol

Aldehydes

cinnamaldehyde
citral

Carboxylic acids

acetic acid
benzoic acid

Chlorinated compounds

chloroform
p-chlorothymol

Esters

ethanol
eugenol
linalool
menthol
methyl salicylate
p-chlorothymol
phenol

Ethers

anethole
butyl ether
eucalyptol
eugenol
vanillin

Hydrocarbons

dipentene
hexane
pinene
toluene

Ketones

acetophenone
camphor
carvone
menthone
methyl isoamyl ketone

TABLE C-2. DILUTE SOLUTION ABSORPTION RESULTS WITH POLYETHYLENE AND POLY(VINYL-CHLORIDE) POLYMERS
(adopted from reference 65)

Organic	Percent loss of organic compound after 1 month[a]	
	Polyethylene	Poly(vinyl chloride)
Menthol	-30	-25
Citral	-53	-30
Methyl salicylate	-69	-20
Carvone	-80	-40
Dipentene	-98	-15
Menthone	-95	-60
Chloroform	-99	-20
Anethole	-100	-75

(a) Experimental conditions :
0.1% by weight organic compound in water-ethanol solution; stored in sealed polymer (PE or PVC) bottle for 1 month at 49°C.

APPENDIX D
CHEMICAL CHARACTERISTICS OF LANDFILL LEACHATES
(adopted from reference 54)

Component or Property	Range of All Values from Garland and Mosher (mg/liter)	Blackwell Forest Preserved Leachate Data from Hughes (mg/liter)	Du Page Leachate Used in Sorption Study (mg/liter)
Total organic carbon	2,566 to 28,000	--	--
Organic acids	--	--	333
Carbonyls as acetophenone	--	--	57.6
Carbohydrates as dextrose	--	--	12
pH	3.7 to 8.5	7.10	6.79
Sulfate	1 to 1,826	680	0.01
Alkalinity ($CaCO_3$)	0.6 to 20,850	3,255	4,220
Chemical oxygen demand	40 to 89,520	39,680	1,362
Biochemical oxygen demand	9 to 54,610	54,650	--
Total solids	0 to 59,200	--	--
Total dissolved solids	0 to 42,276	19,144	5,910
Total suspended solids	6 to 12,685	--	--
Electrical conductivity (mohms/cm)	3 to 17	10.90	7.20
Hardness ($CaCO_3$)	0 to 22,800	7,830	1,100
Total phosphates	0 to 154	6	0.1
Ortho-phosphate	6 to 85	--	--
NH_4-N	0 to 1,105	--	809
NO_3 + NO_2 - N	--	1.70	--
Aluminum	--	2.20	0.1
Arsenic	--	4.31	0.11
Boron	--	--	33
Cadmium	0 to 17	0.05	0.01
Calcium	5 to 4,080	--	49
Chlorine	34 to 2,800	1,697	1,070
Chromium	--	0.20	0.1
Copper	0 to 10	0.05	0.1
Iron	0 to 5,500	5,500	4.40
Lead	0 to 5	--	0.1
Magnesium	16 to 14,600	--	204
Manganese	0 to 1,400	1.66	0.1
Mercury	--	--	0.0008
Nickel	--	--	0.3
Potassium	3 to 3,770	--	516
Silicon	--	--	15.1
Sodium	0 to 7,700	900	822
Zinc	0 to 1,000	--	0.03